Electronic Structure and Charge Tranfer in Nanosystems with Ab initio Calculations

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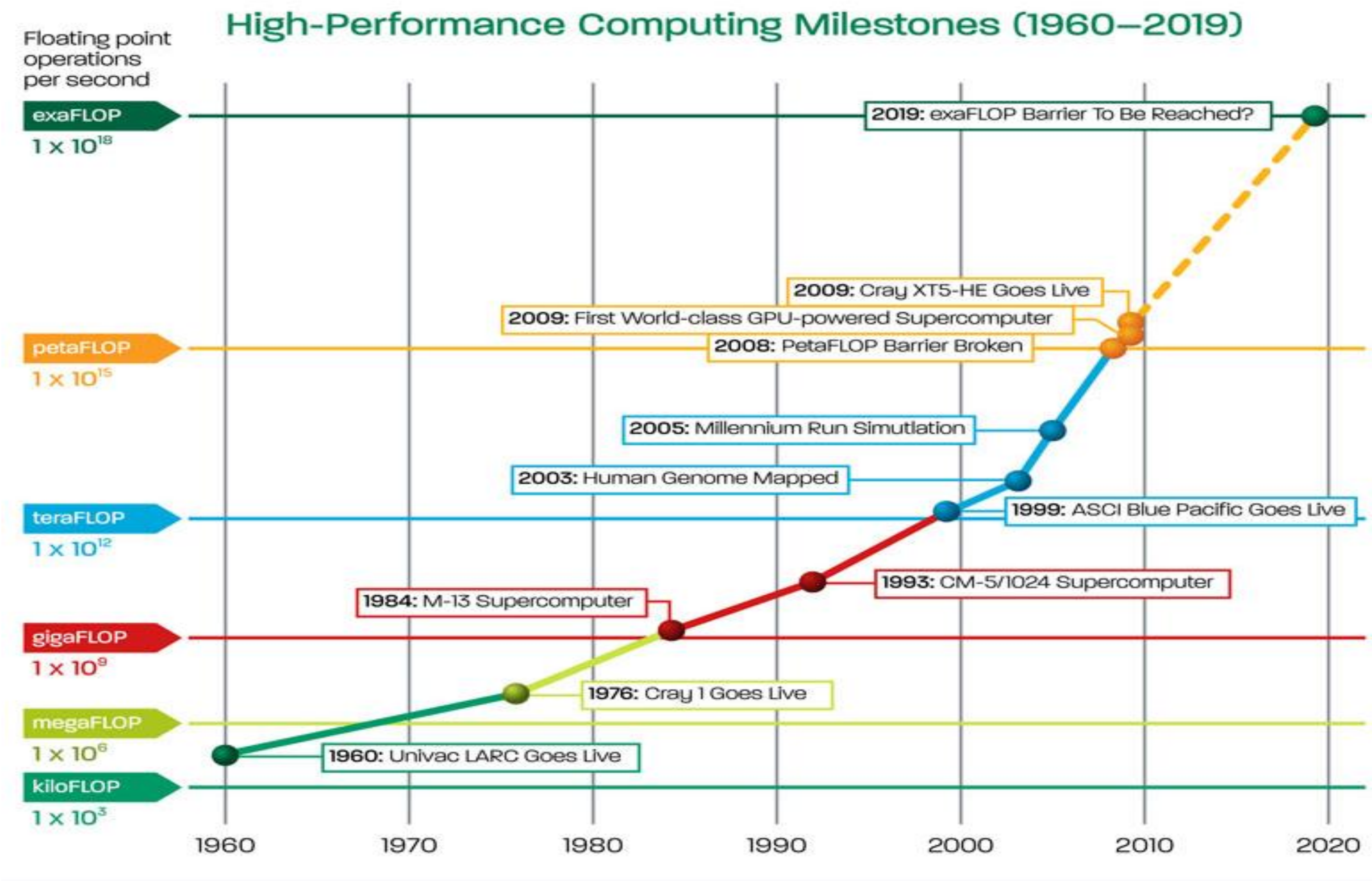
US Department of Energy
BES, Office of Science

INCITE Project
NERSC, NCCS, ALCF

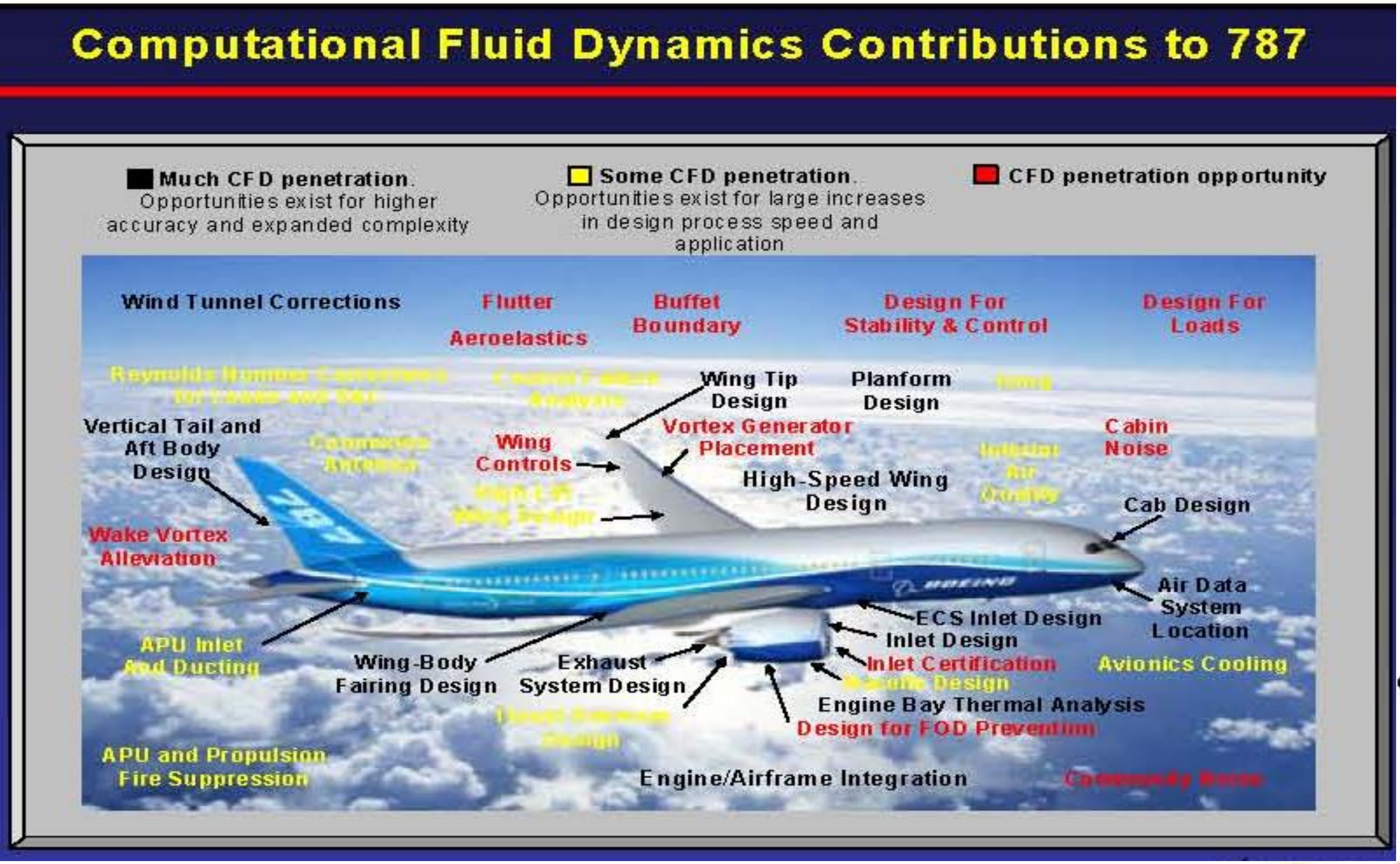
~ 50,000 times computer speed increase in last 20 years



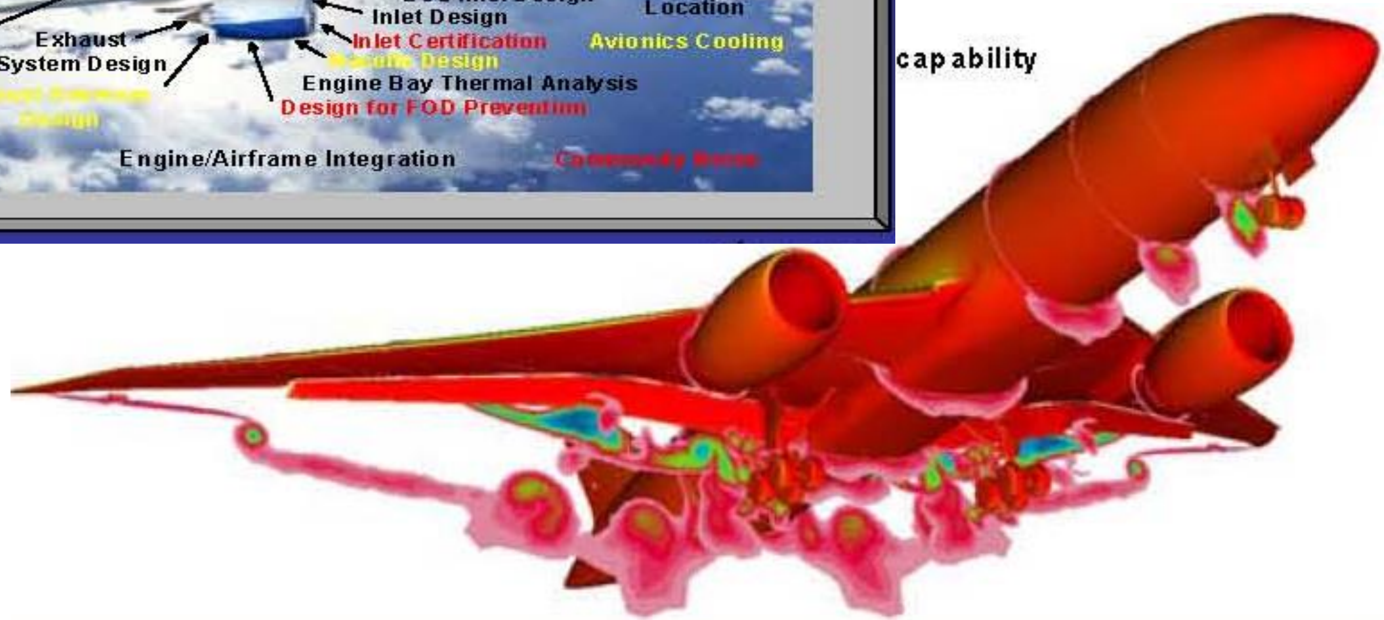
one job, 50,000 cores for 10 hours = 57 years on one desktop!

Much of the improvement comes from parallelization → Change software

Computational Fluid Dynamics + HPC



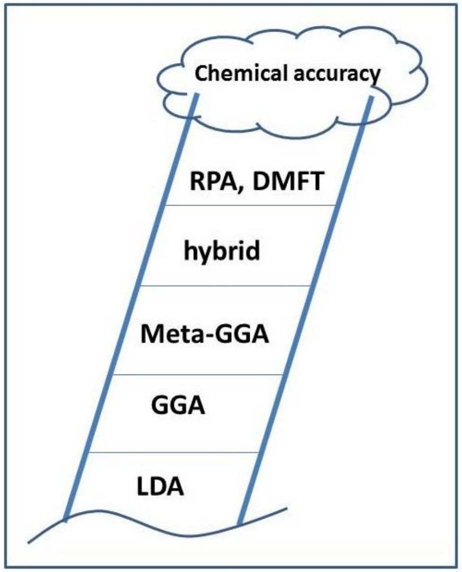
capability



Three main challenges for ab initio material simulations

(1) **Accuracy**

(climb Jacob's ladder)



(2) Temporal scale (from fs to seconds)

(new algorithms, like the accelerated MD)

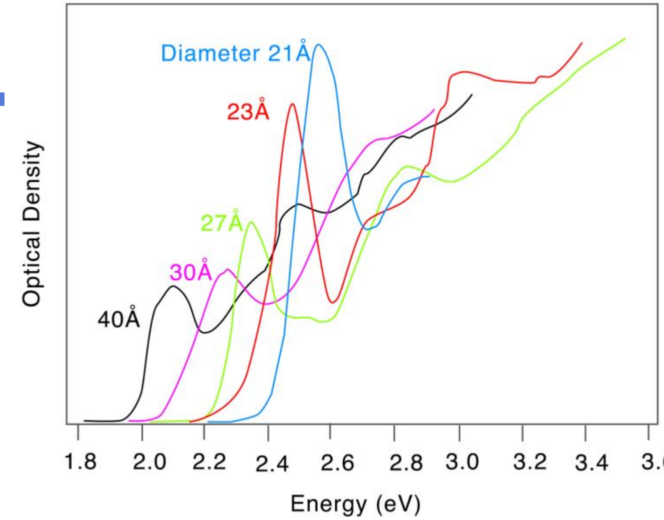
(3) Size scale (mesoscale problems)

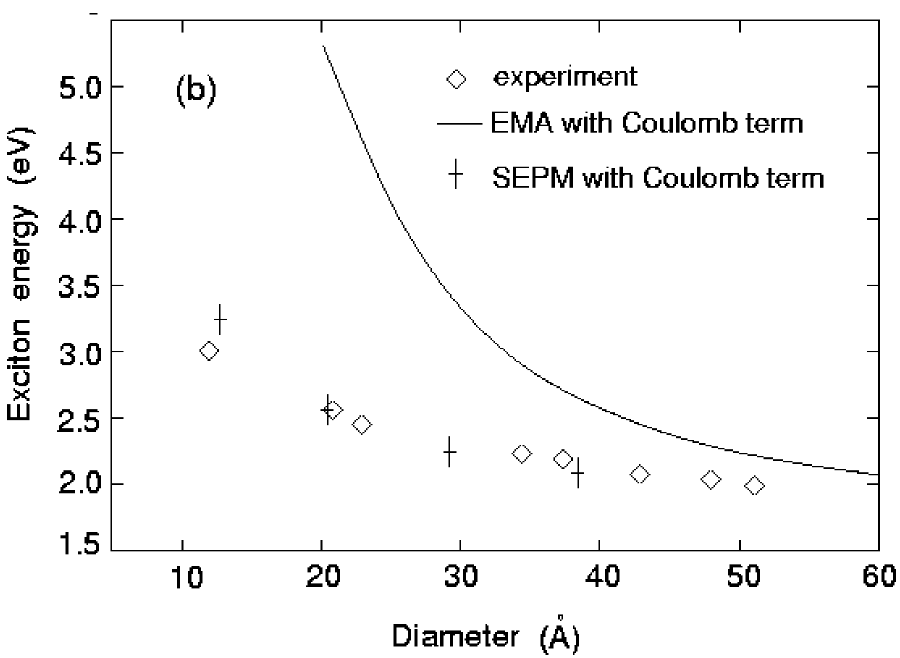
(Divide & Conquer methods)

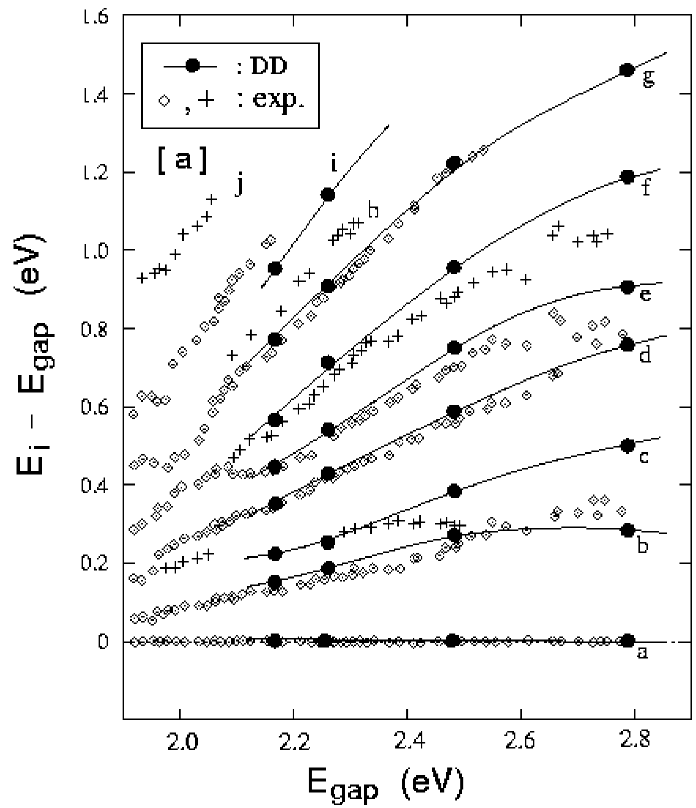
All can be helped by exascale computing

L.W. Wang, Divide and conquer quantum mechanical material Simulations with exascale supercomputers, Nat. Sci. Rev. 2014.

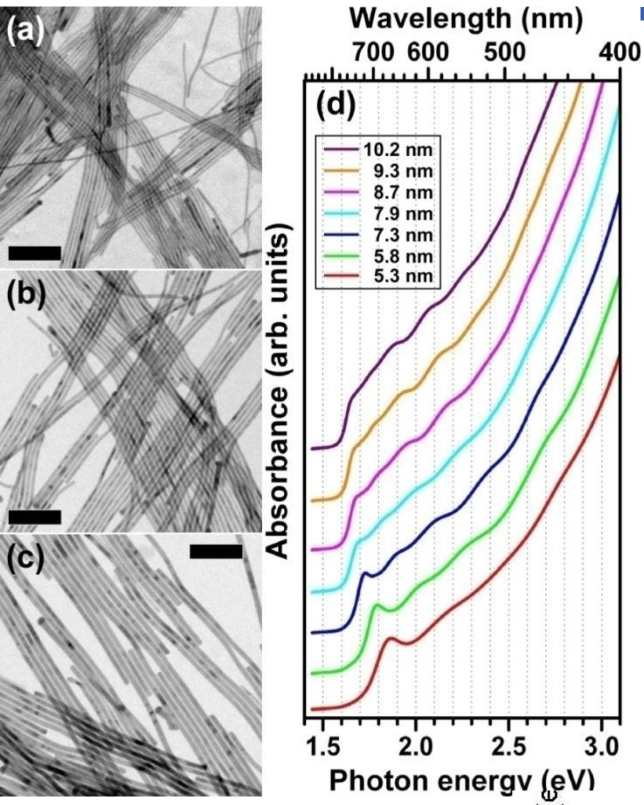
CdSe quantum dot results





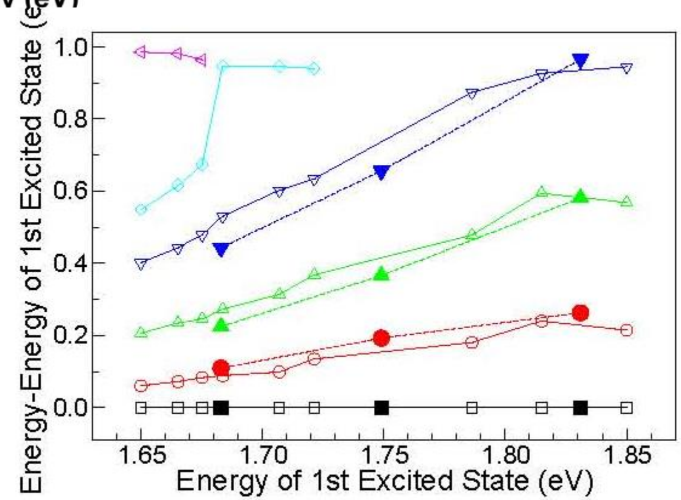


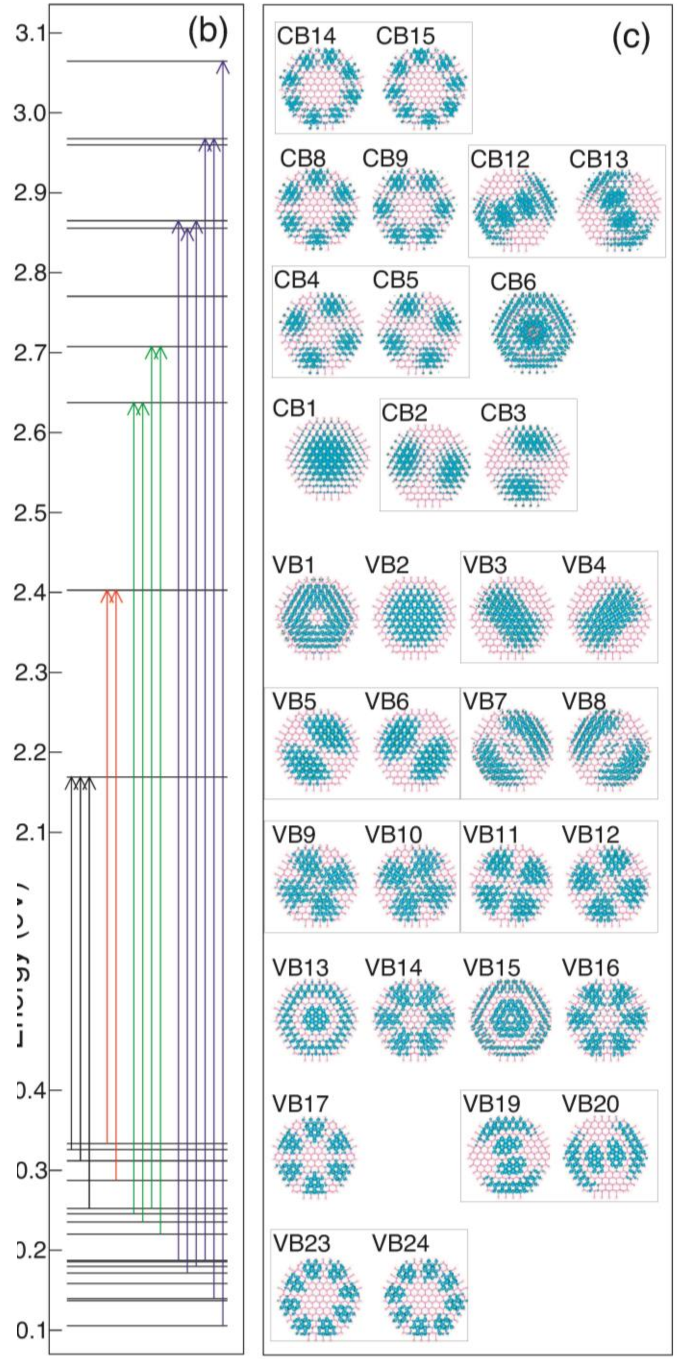
CdTe nanowire



Exp:

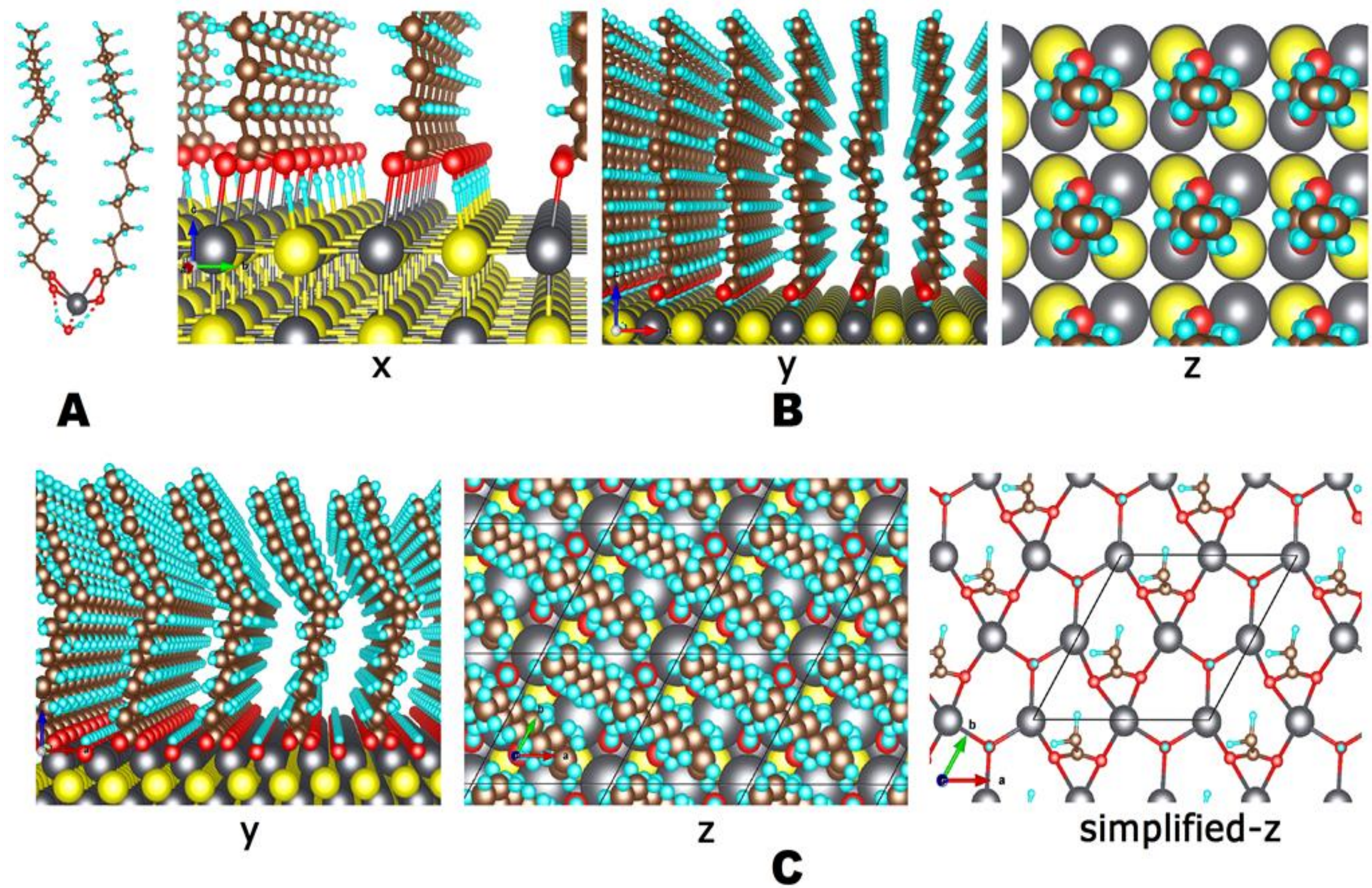
Calc:





Surface passivation of PbS

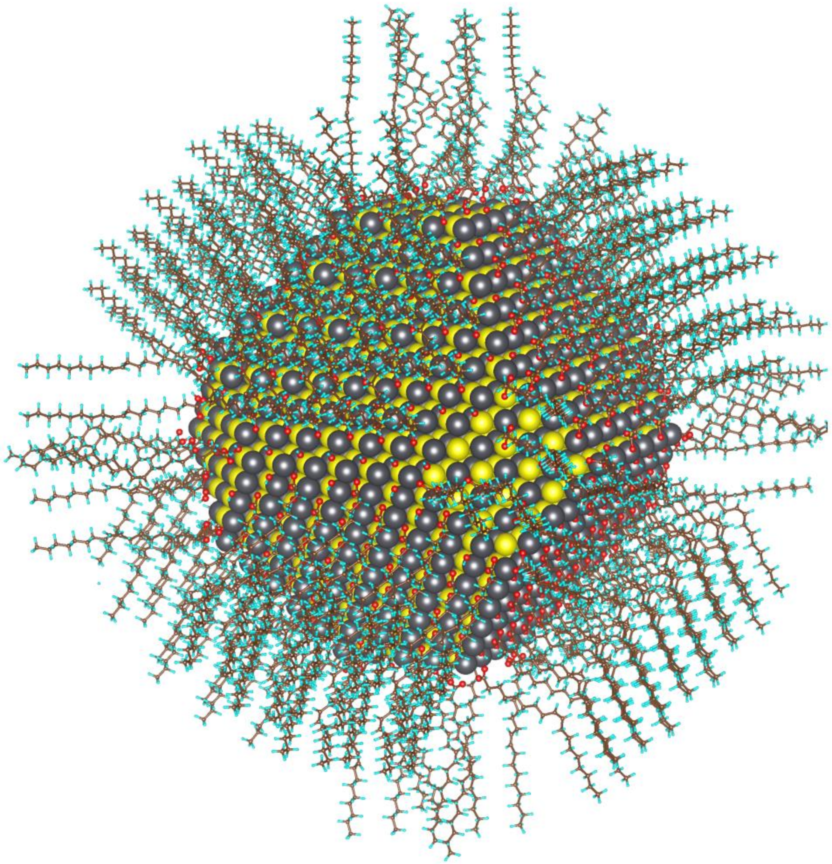
Oleic acid

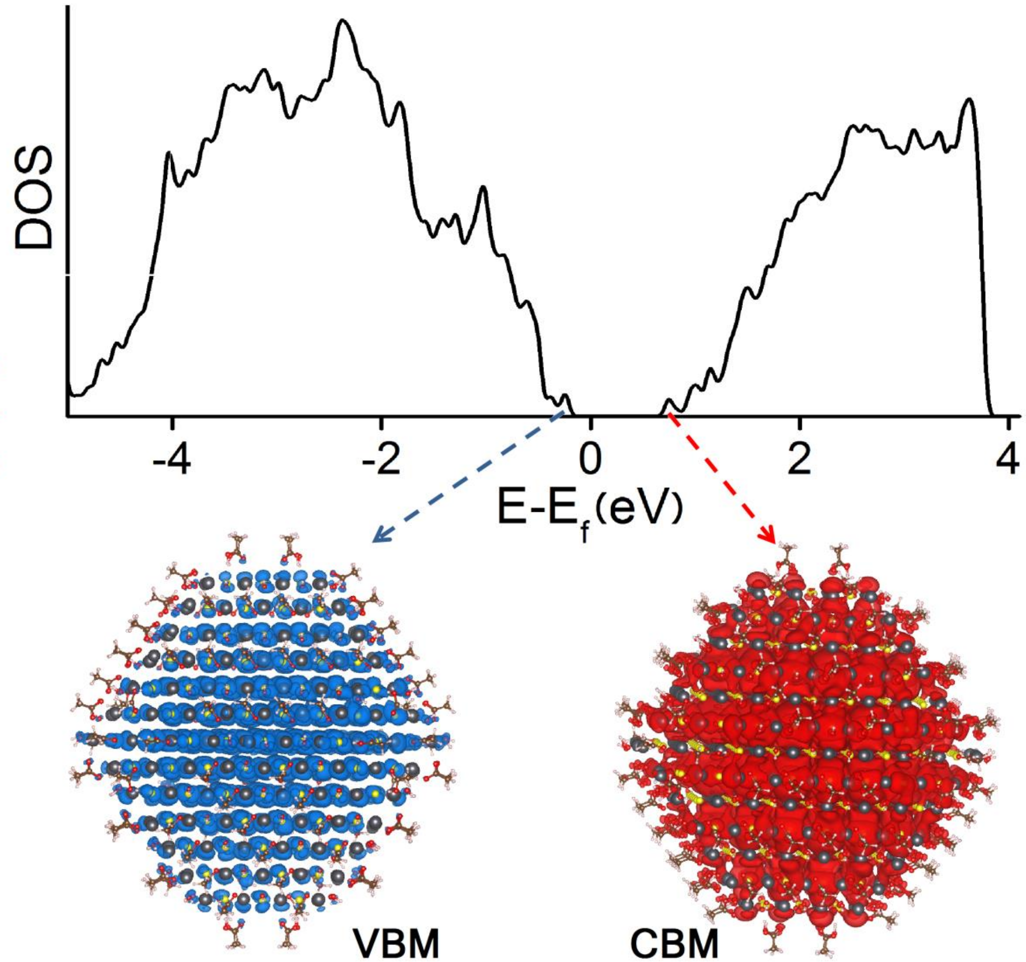


PbS (001)

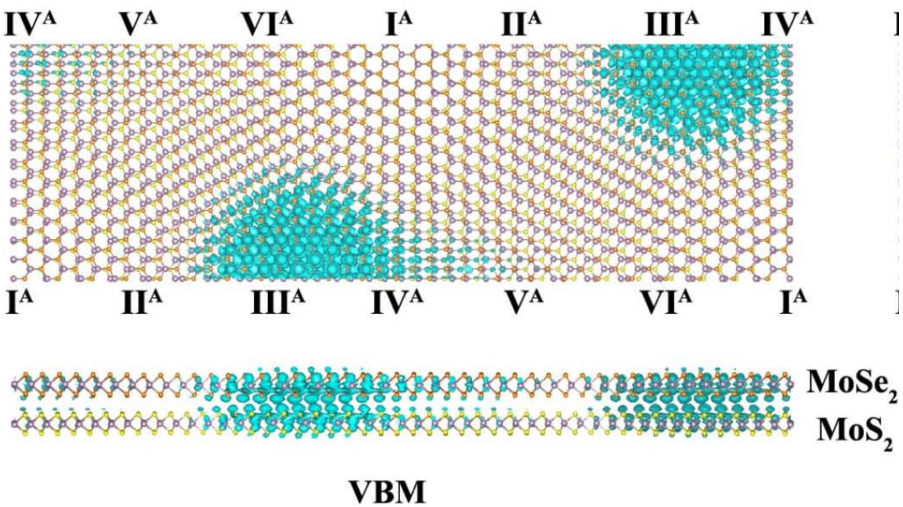
PbS (111)

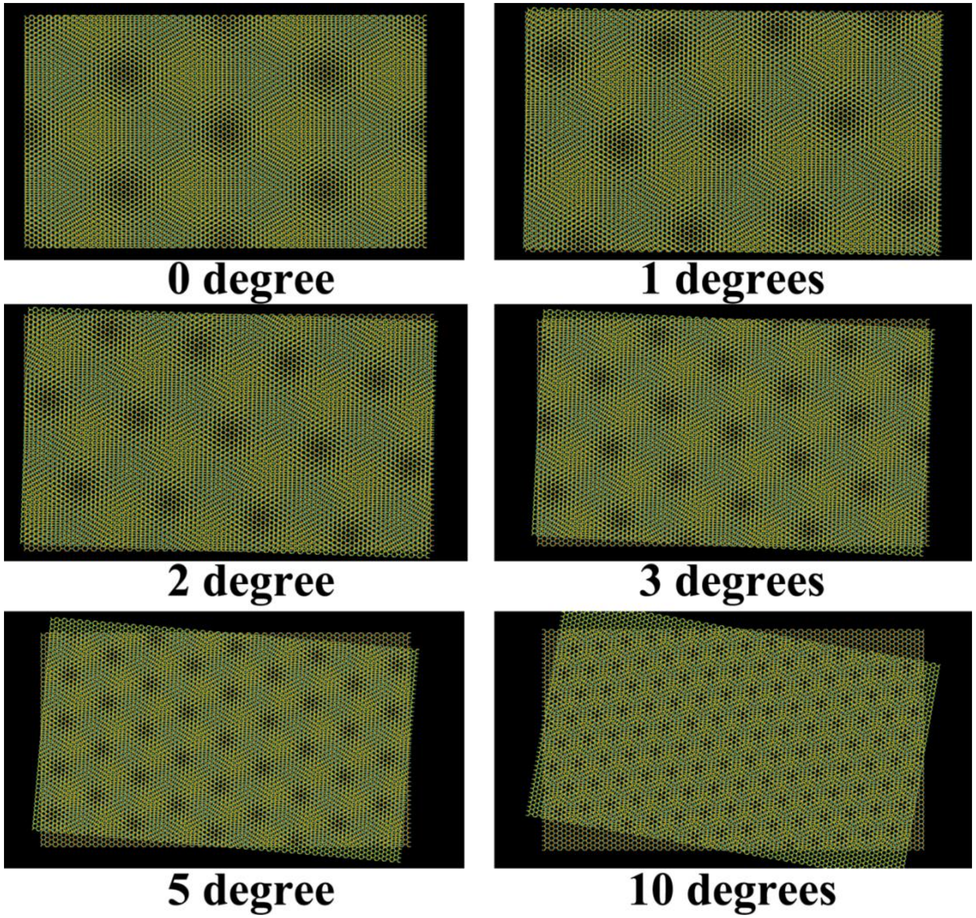
An atomistic model which fits all the exp. facts



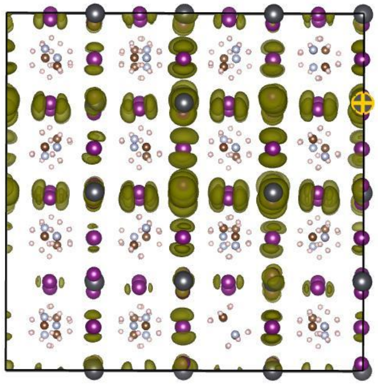
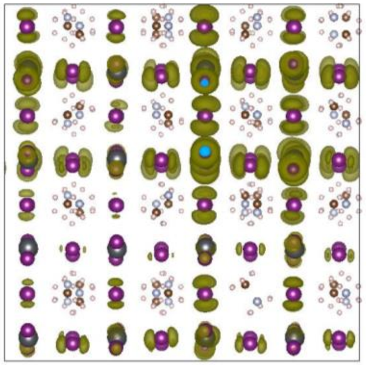


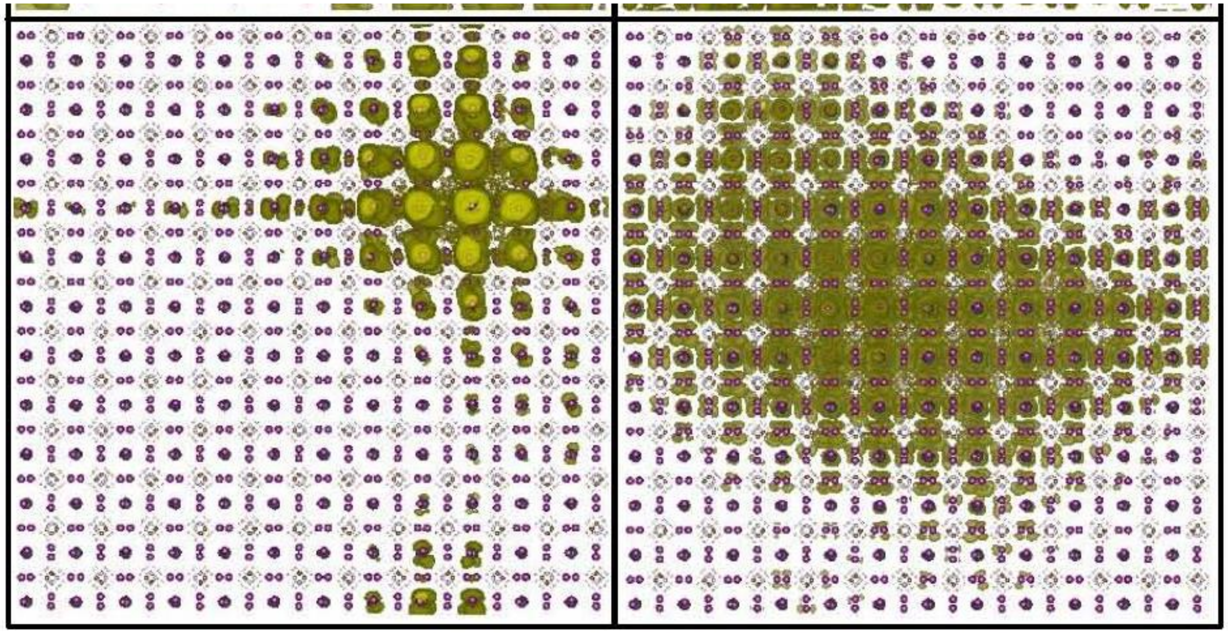
Carrier localization in MoS_2-$MoSe_2$





LS3DF: Hybrid (CH3NH3)PbI_3 perovskite for solar cell

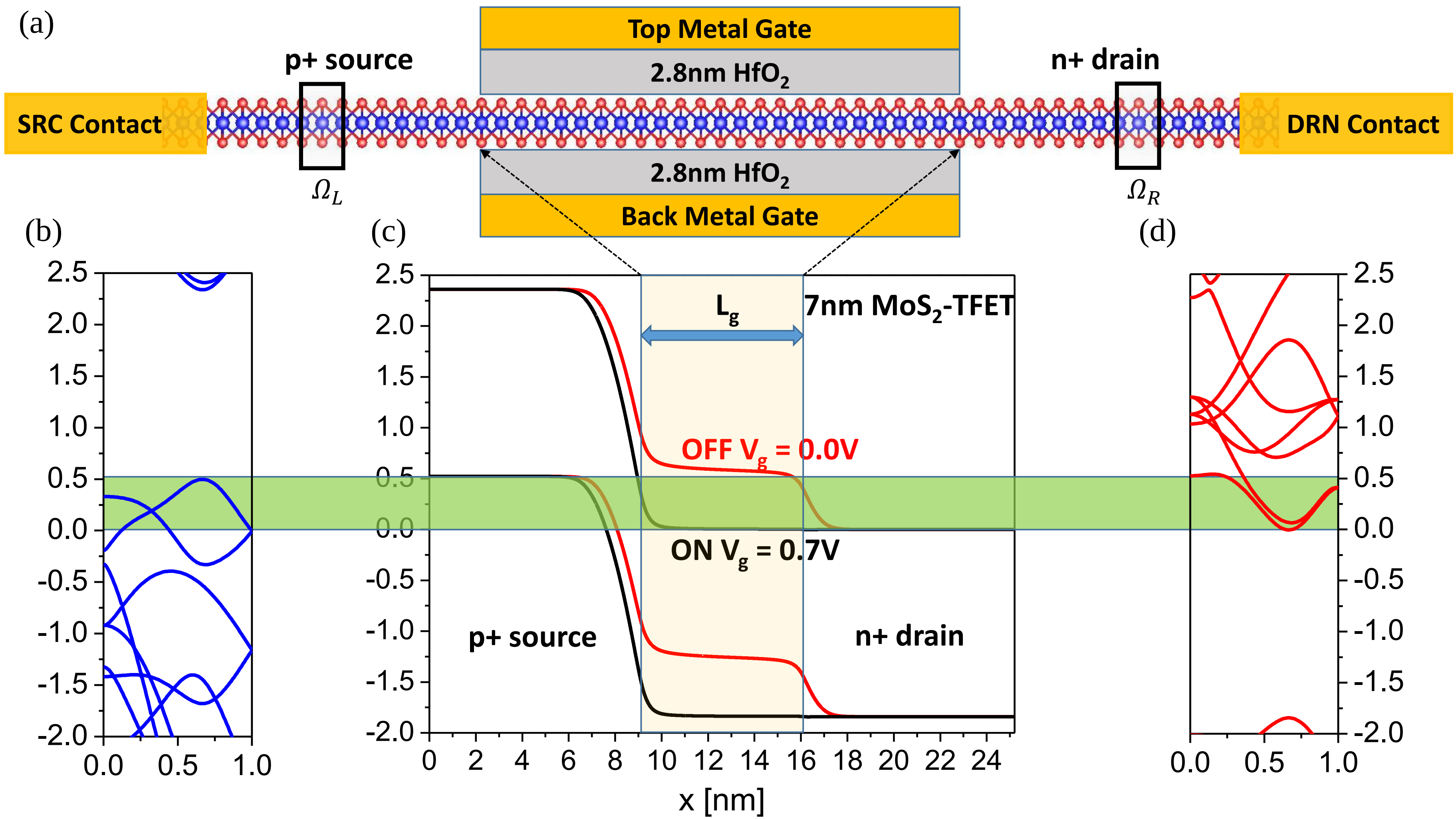
LS3DF   Direct DFT ~700 atom



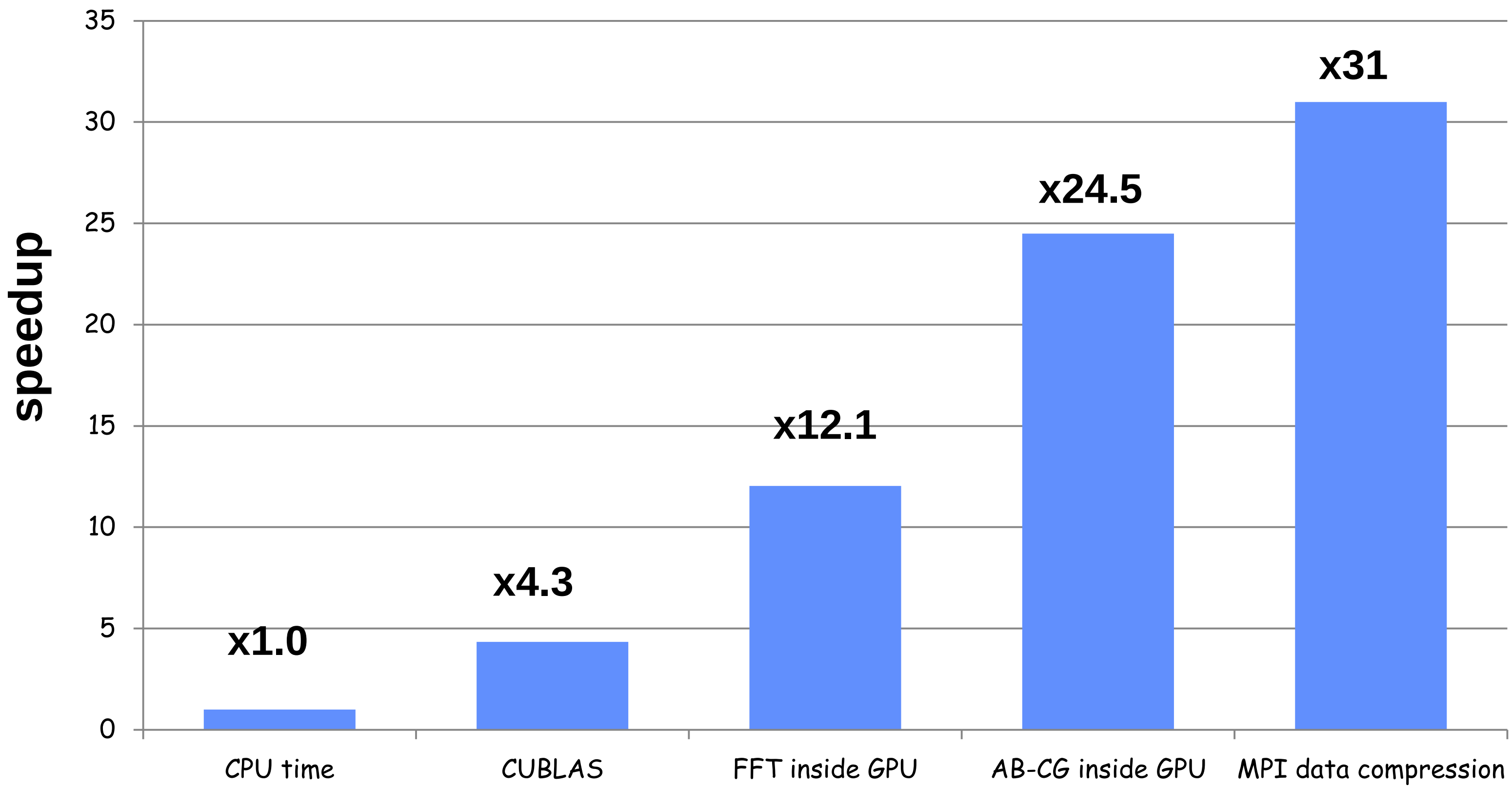
~20,000 atoms

CBM VBM

MoS_2 for Tunnel FET

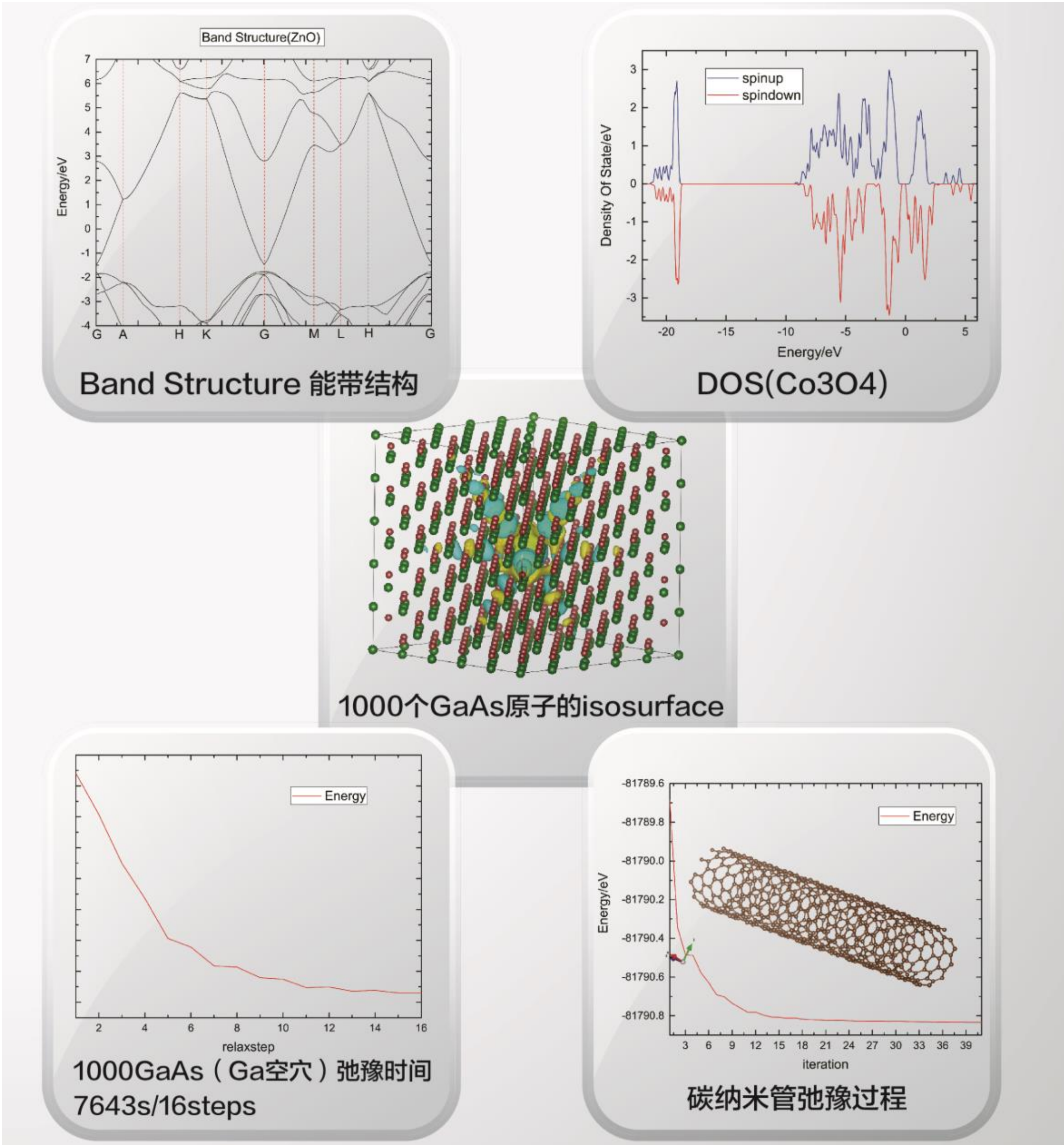


GPU speedup of PW code (e.g., PWmat)



The speedup of GPU CG_AllBand over CPU PEtot code on Titan.

PW GPU calculation can be very fast



1000 atom (GaAs) atomic relaxation for 2 hours on a 4 GPU workstation (PWmat+Mstation).

A few approaches for charge transfer/transport calc.

- **Elastic transport (NEGF, or Scattering state)**
- **Bloch state scattering (electron-phonon, electron-defects)**
- **Single phonon assisted localized state hopping (electron-phonon)**
- **Multiple phonon assisted hopping**

  (1) Classical treatment: Marcus theory
  (2) Quantum formalism: electron-phonon coupling

- **Direct simulation: nonadiabatic MD**

Outline

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- ❖ Quantum mechanical formalism for multi-phonon process (L. Shi)
- ❖ Nonadiabatic MD simulation for large organic systems (J.F. Ren)
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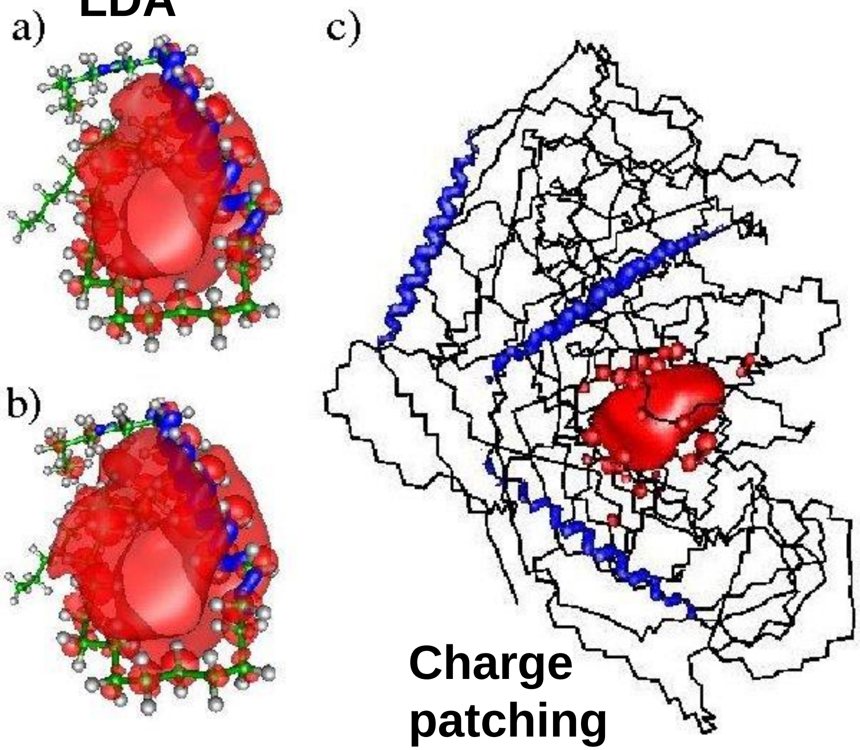
Charge patching for organic molecules

Direct LDA



Charge patching

Charge patching

Red: LUMO (CBM); Blue: HOMO(VBM)

Long Alkane chain.

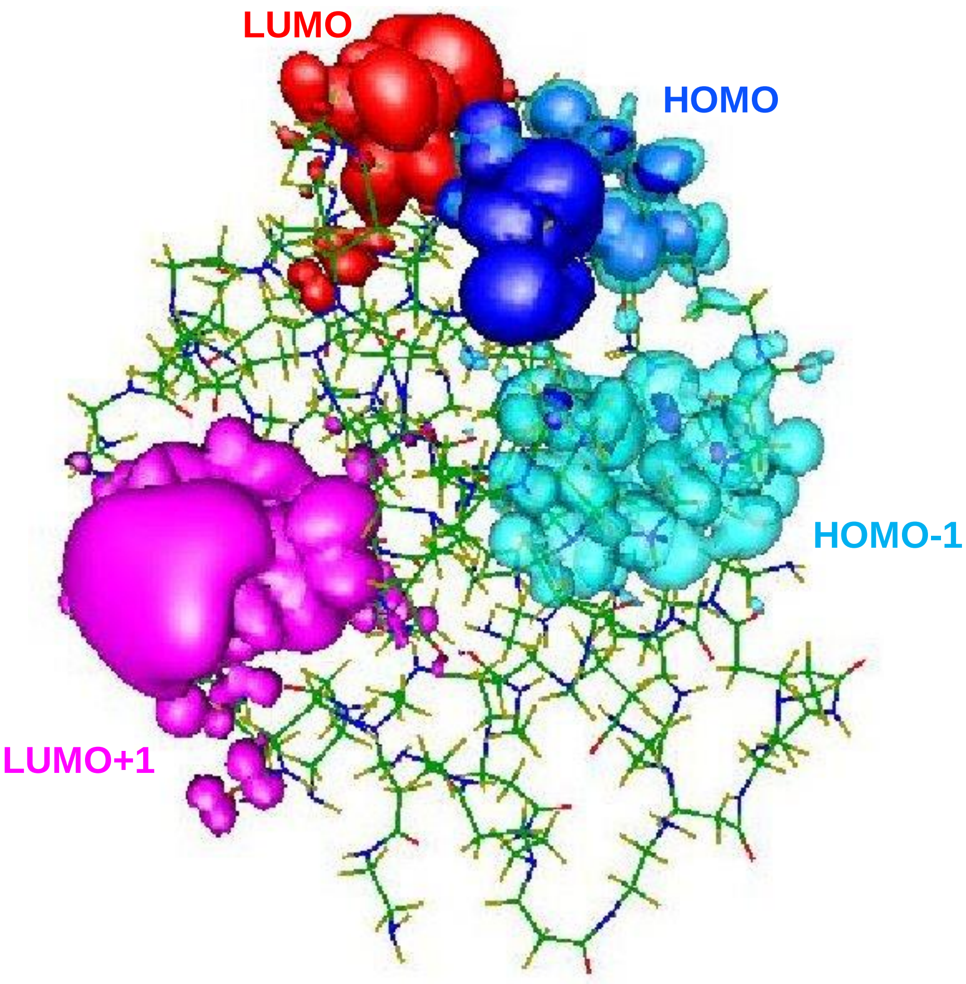
Tested:

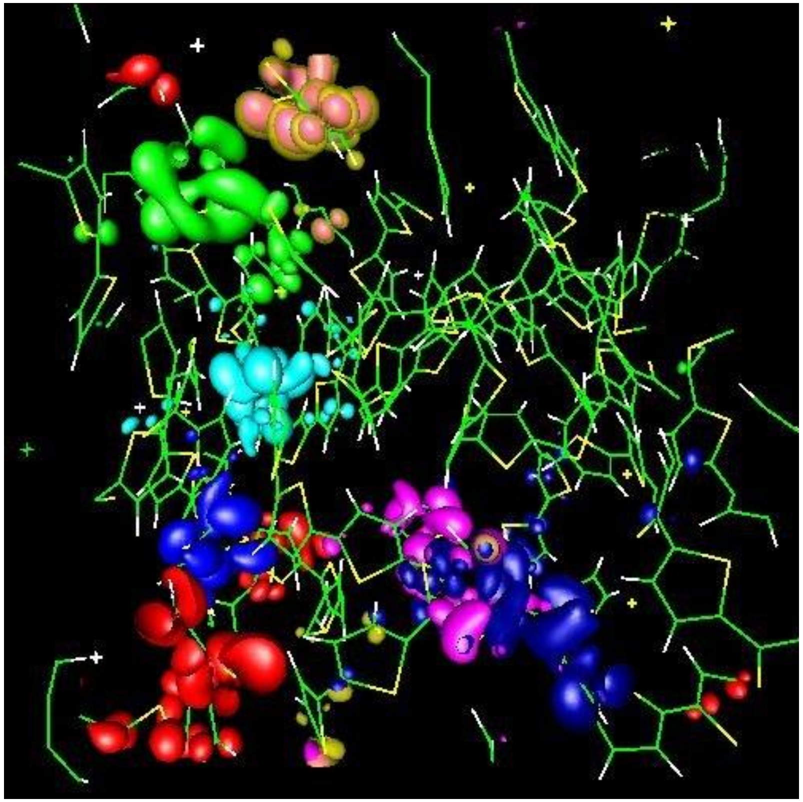
alkanes, alkenes, acenes thiophenes,furanes,pyrroles, PPV

Different length and configurations

Typical eigen energy error is less than 30 meV

Electron states in other organic systems (charge patching)

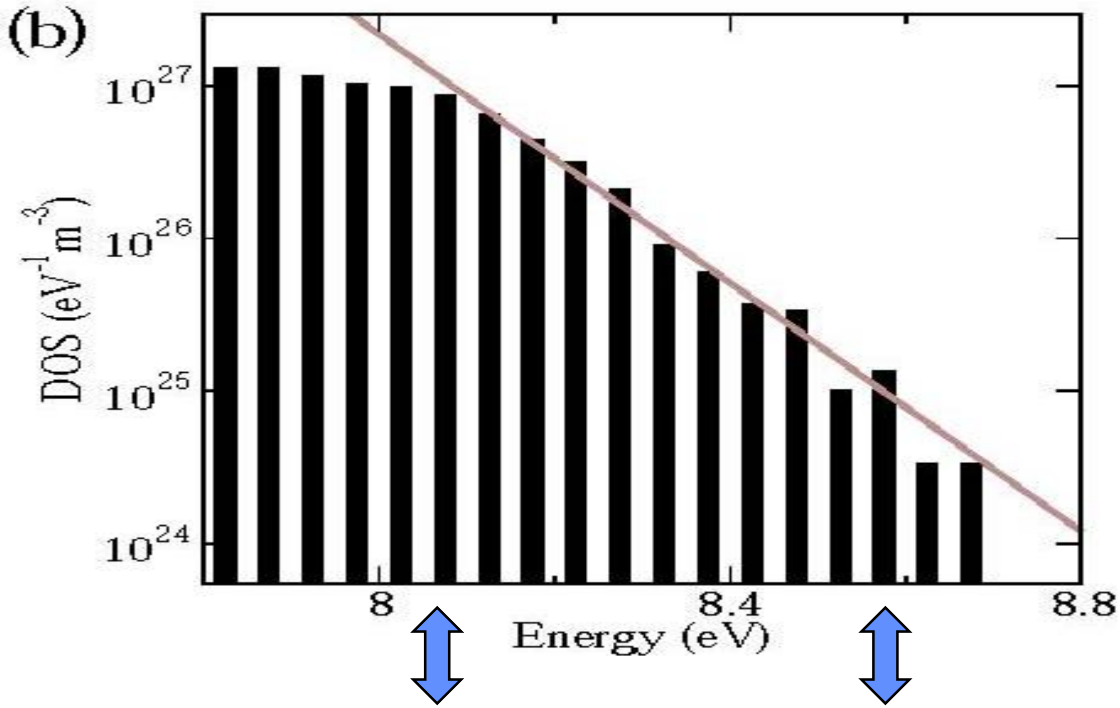


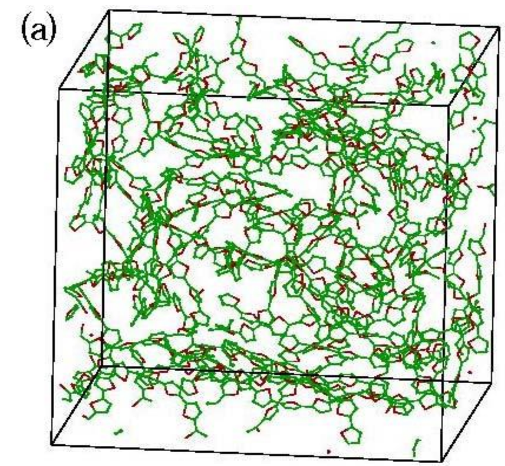


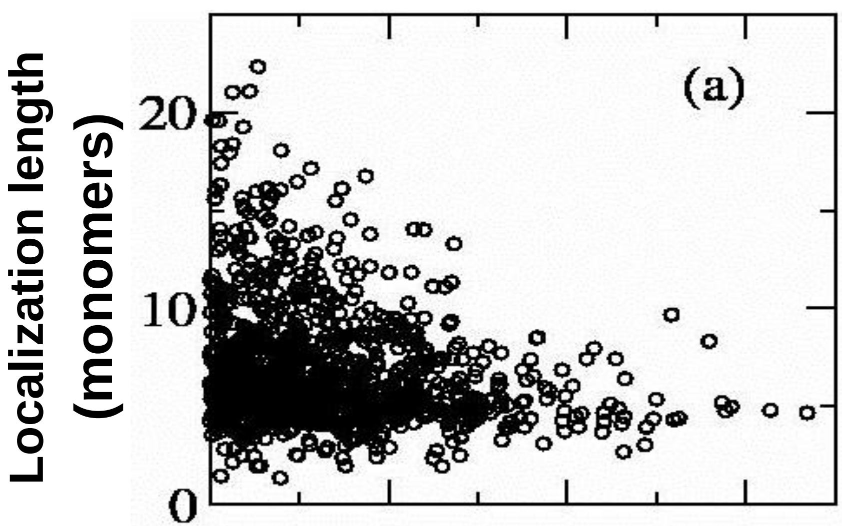
An amorphous P3HT blend

A 3 generation PAMAM dendrimer

The tail of the density of states







Averaged over 50 configurations (MD snapshots), and each with 10,000 atoms.

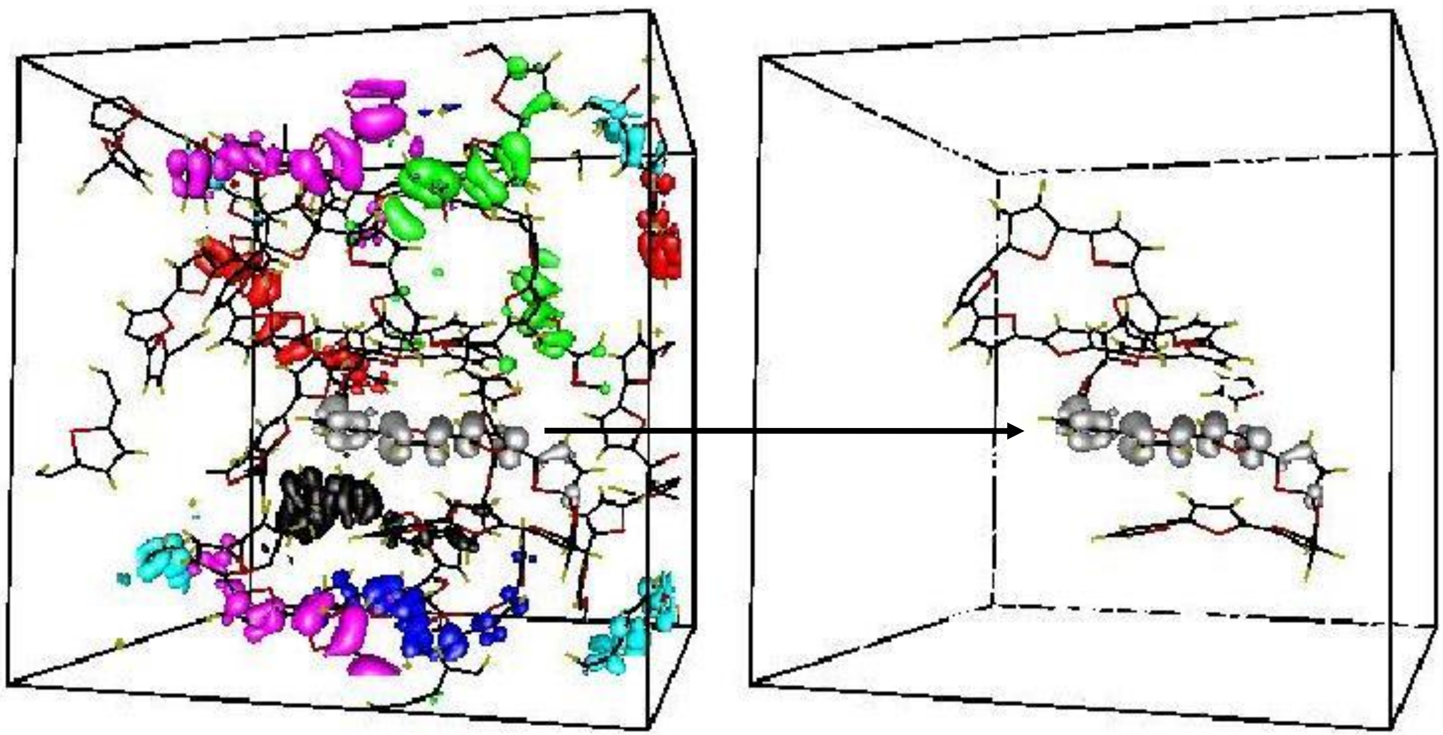
$$L = \frac{1}{\int \psi^4 d^3 r}$$

Hole Wave functions in P3HT

- typically localized to 3-6 rings.
- weakly affected by other chains.

P3HT – 5 chains with 20 rings (2510 atoms)

blue: 18.910eV
green: 18.888eV
cyan: 18.755eV
red: 18.690eV
pink: 18.682eV
black: 18.675eV
white: 18.654eV



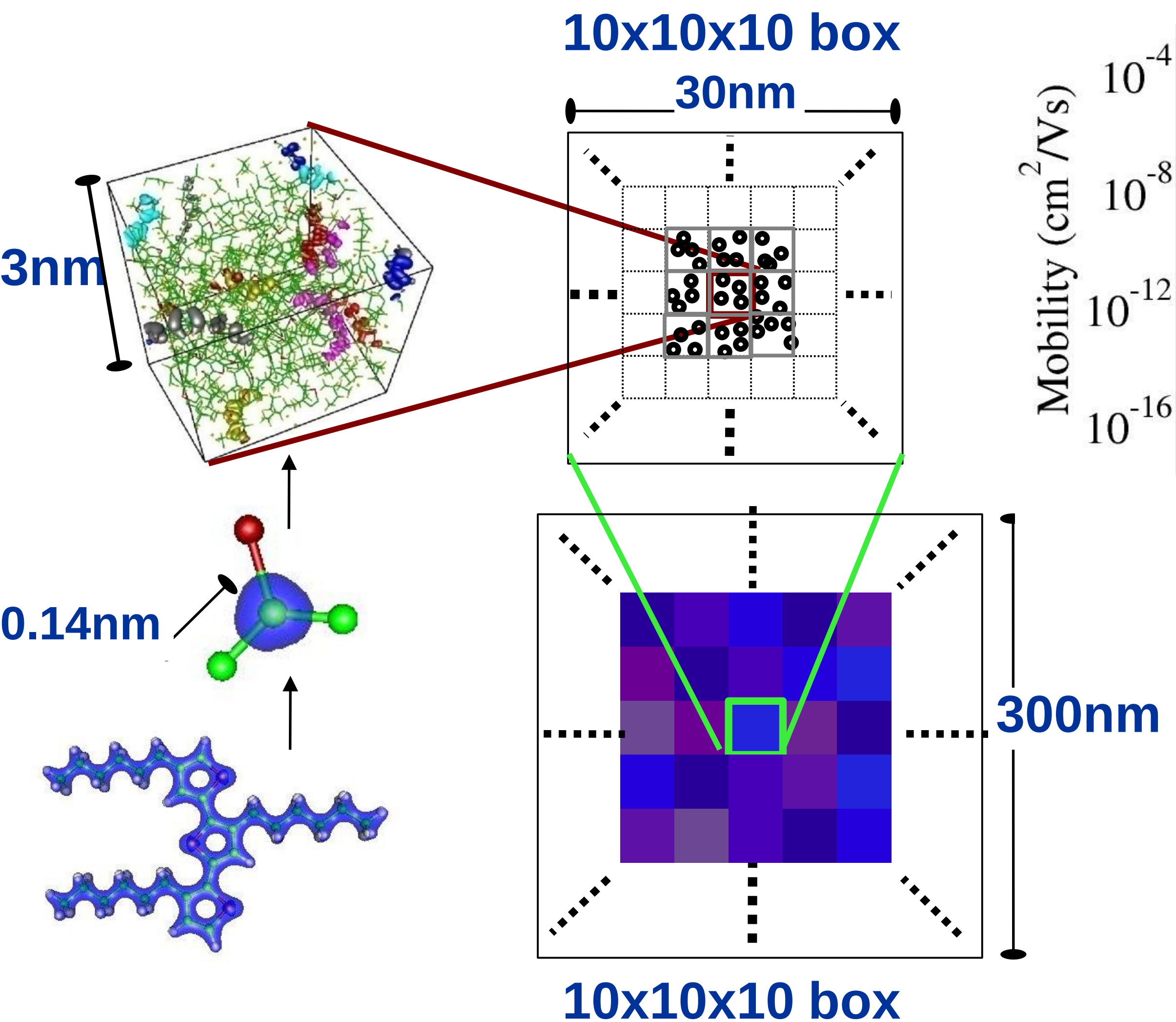
Explicit calculation of localized states and their transition rates

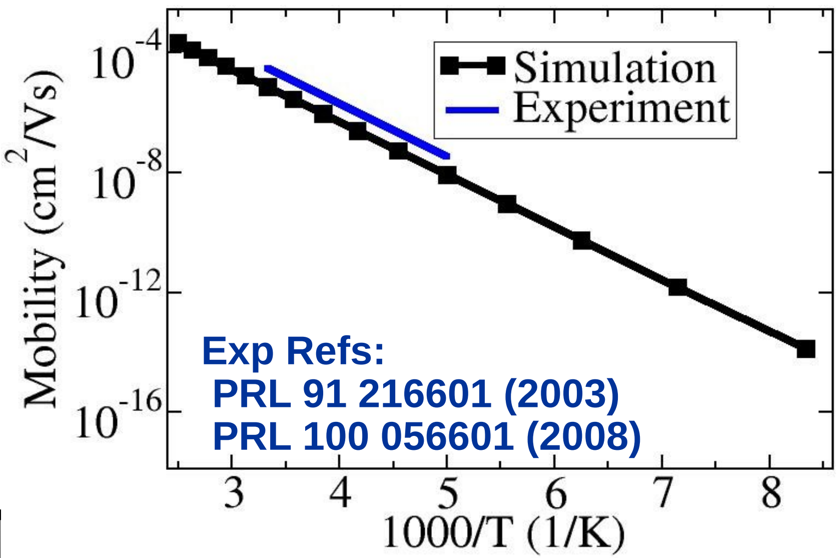
- ❖ **Classical force field MD for P3HT blend atomic structure**
- ❖ **Take a snapshot of the atomic structure**
- ❖ **CPM and FSM to calculate the electronic states ψ_i.**
- ❖ **Classical force field calculation for all the phonon modes**
- ❖ **Quick CPM calculation for electron-phonon coupling constants** $C_{i,j}(\upsilon) = \langle \psi_i | \partial H / \partial \upsilon | \psi_j \rangle$
- ❖ **transition rate W_{ij} from $C_{ij}(v)$:**

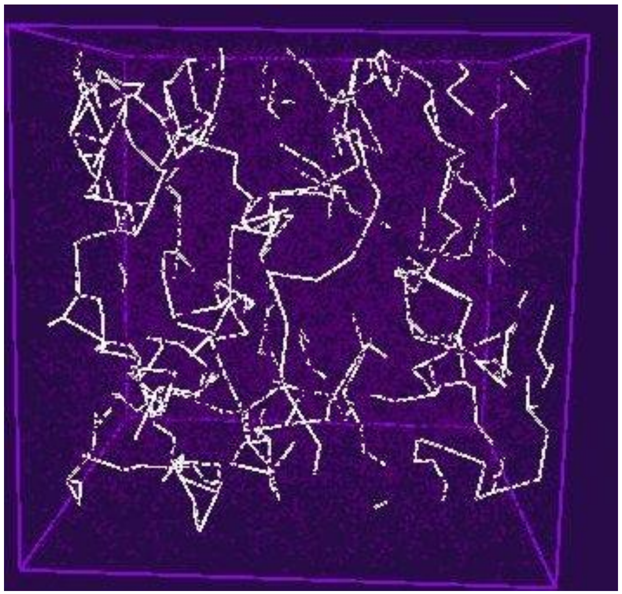
$$W_{ij} = \sum_{\nu} | C_{ij}(\nu) |^2 [n_\nu + 1/2] \delta(\varepsilon_i - \varepsilon_j - \hbar\omega_\nu) + ..$$

- ❖ **using W_{ij} and multiscale approach to simulate carrier transport**

Multiscale model for electron transport in random polymer







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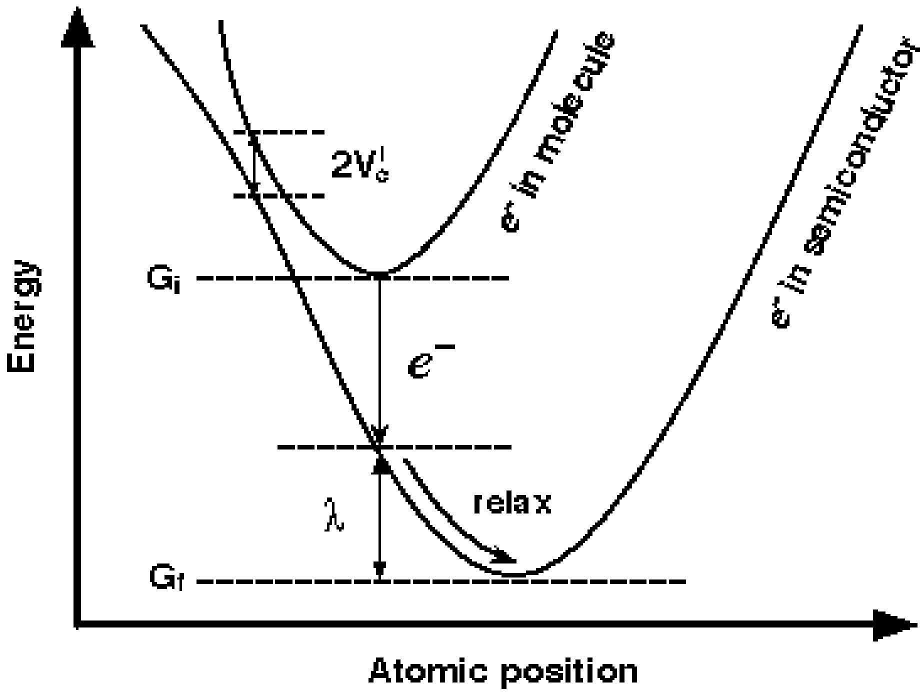
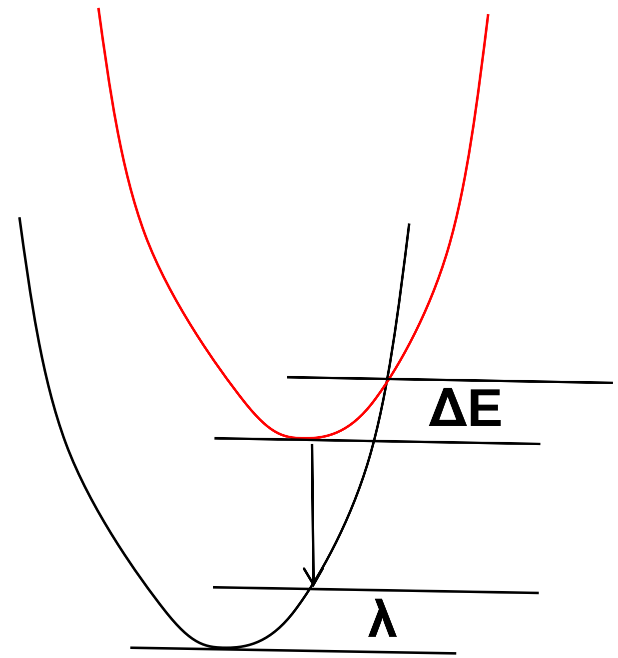
Marcus theory calculation for charge transfer

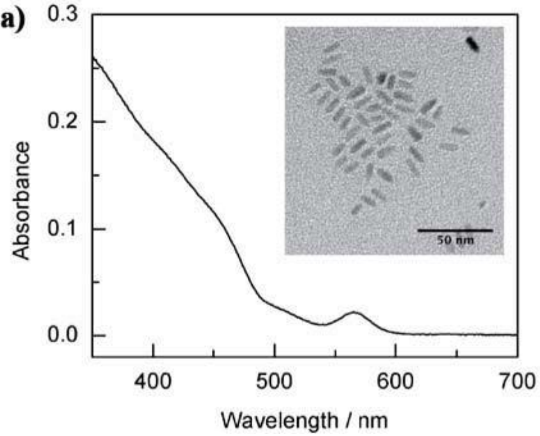


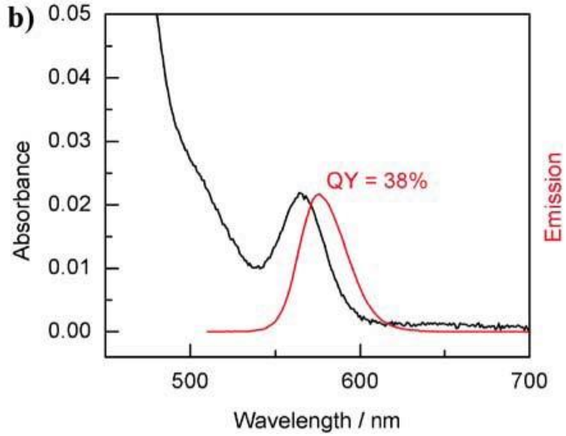


$$Rate = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k T \hbar}} \underbrace{\exp[-(\lambda + \varepsilon_a - \varepsilon_b)^2 / 4\lambda k T]}_{\exp(-\Delta E/kT)}$$

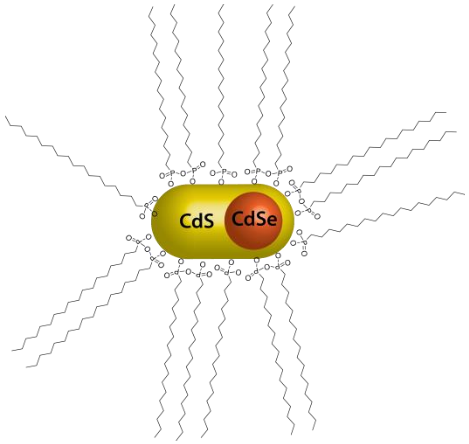
Landau-Zener rate

The experiments



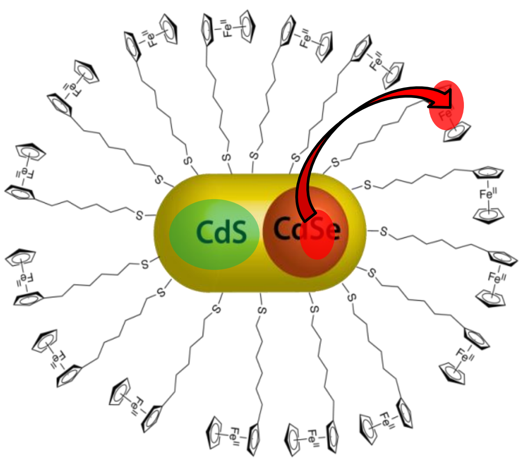


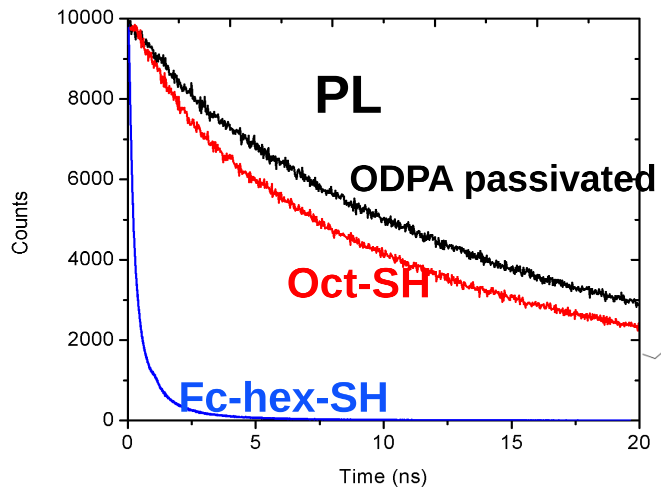
ODPA passivated



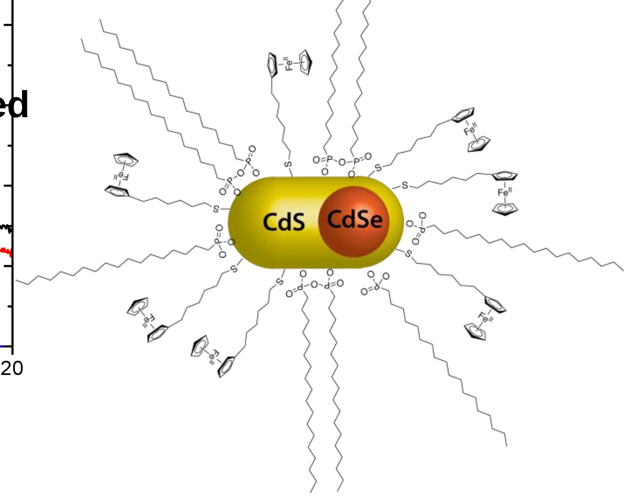
4.4nm wide /11 nm long CdSe/CdS core seeded nanorod

Ligand exchange

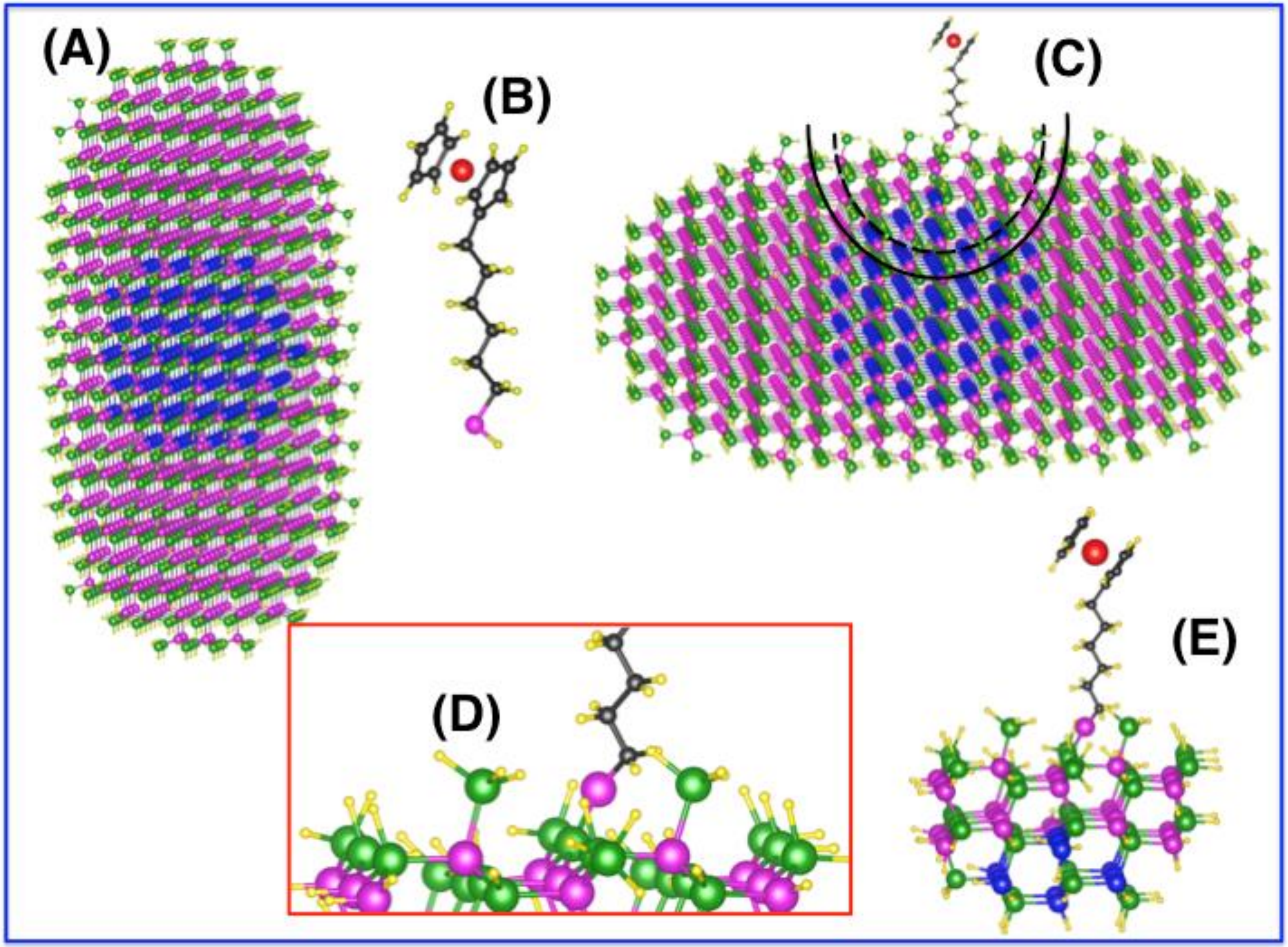




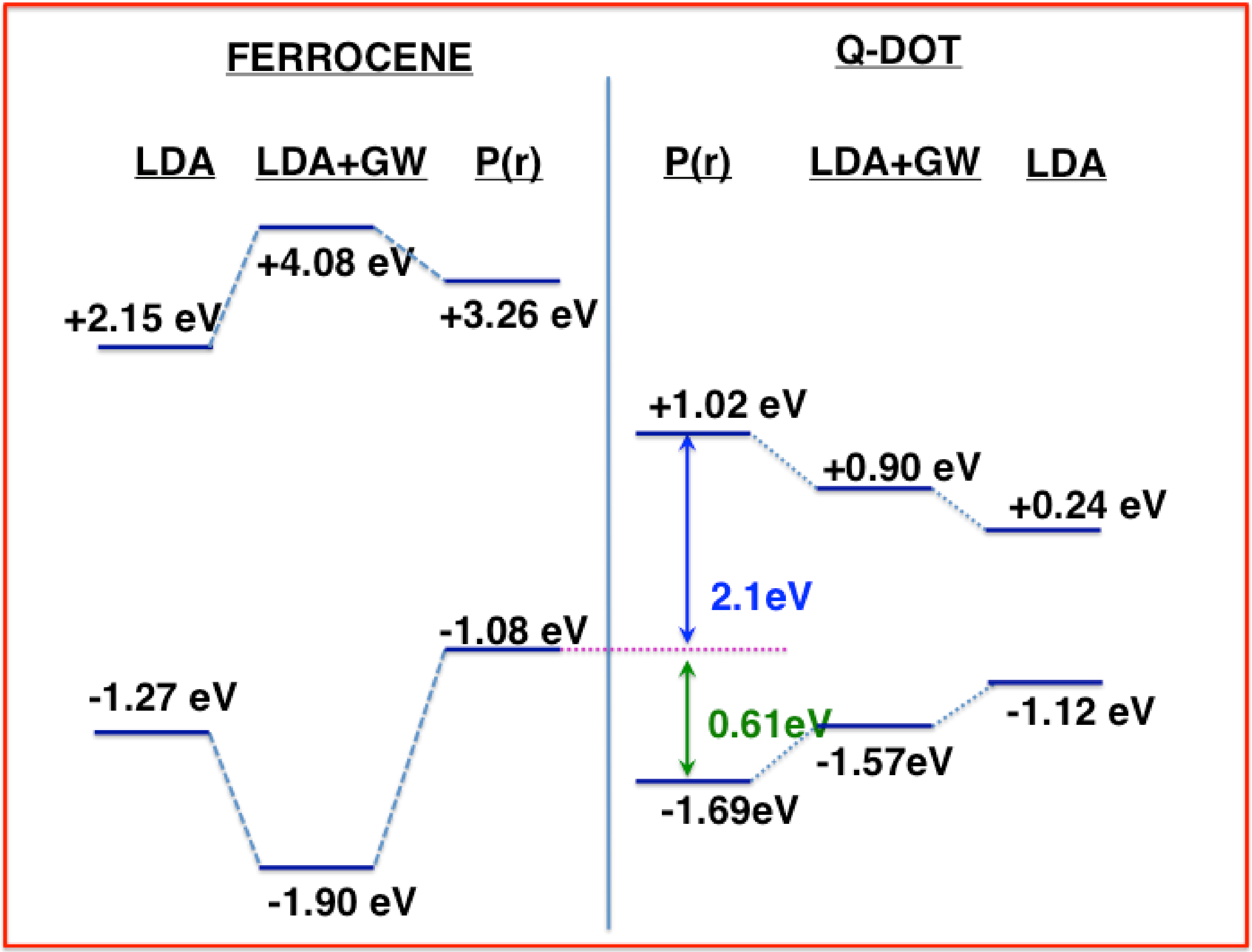
Fc-hex-SH passivated



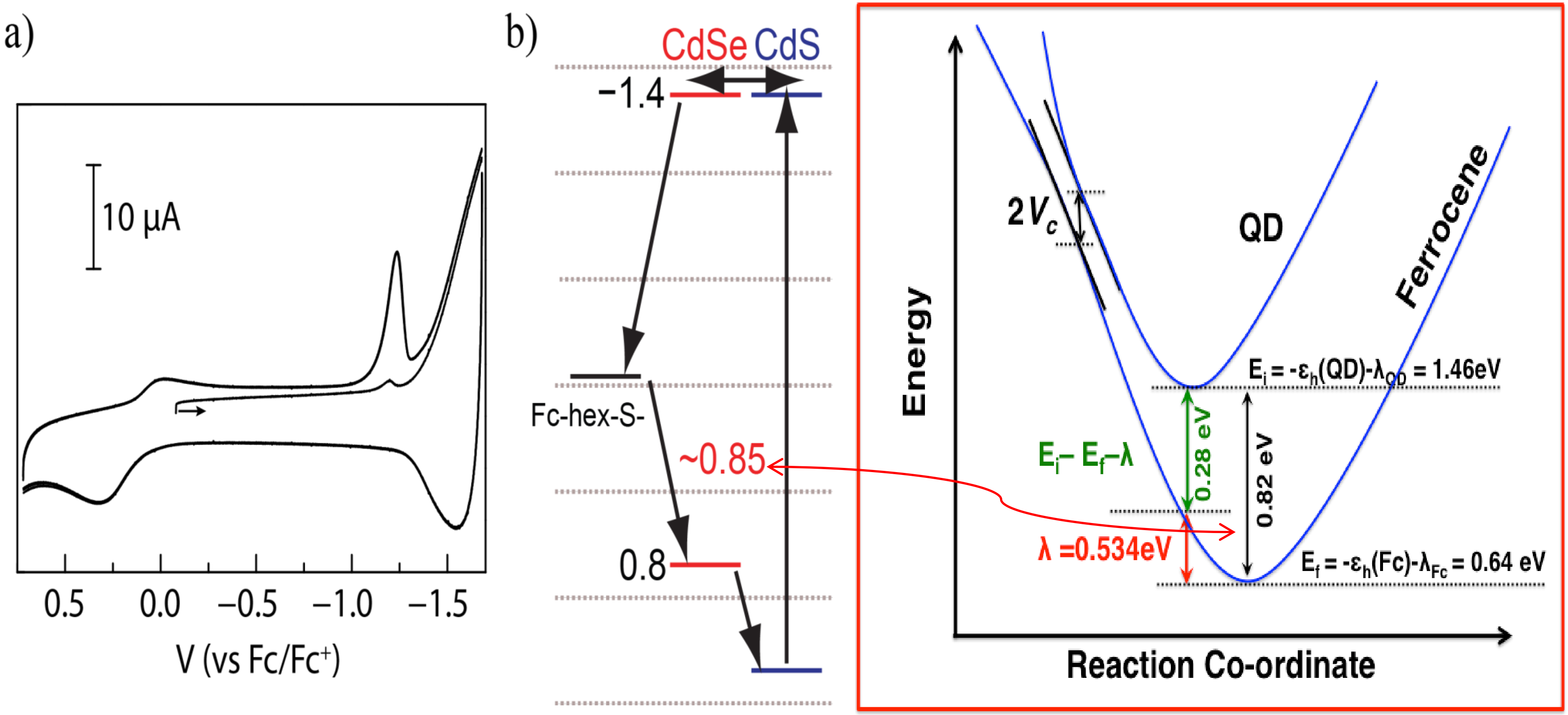
CdSe/CdS-Ferrocene system



Band alignment LDA + GW correction



Quasi particle energy and Marcus diagram

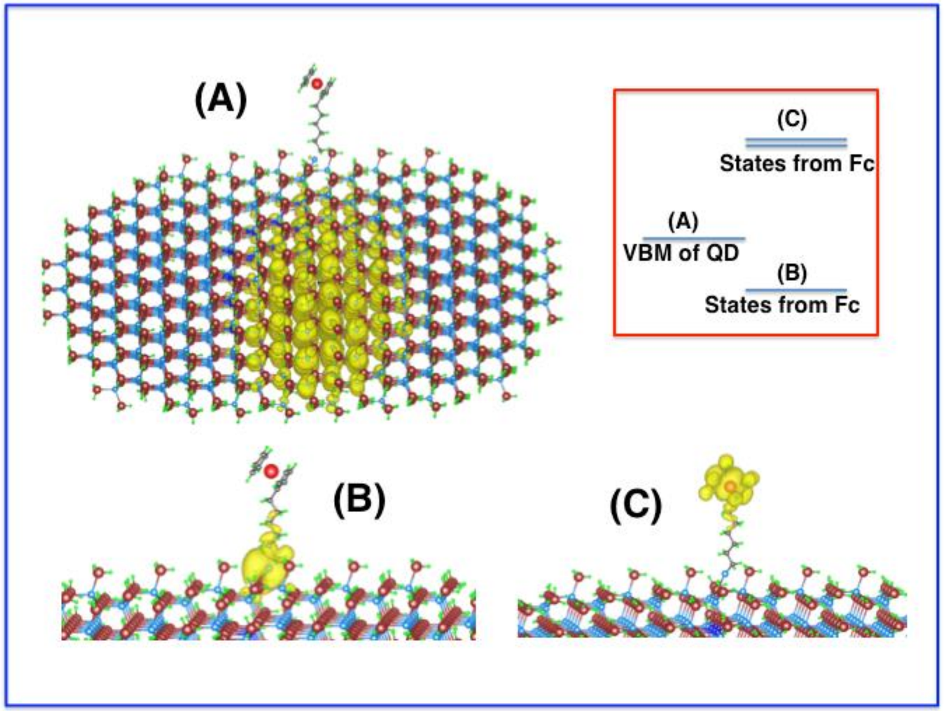


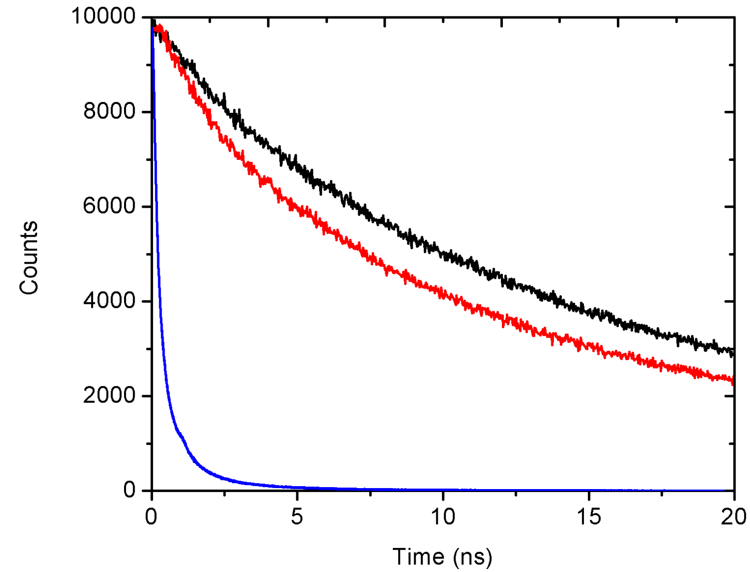
system	λ_{cc}^{at}	λ_{cc}^{sol}	λ_{CT}^{sol}
Ferrocene	48	390	348
QD	138	93	**(meV)**

$$E_i = E(N) - [\epsilon_h(QD) + \lambda_{QD}]$$

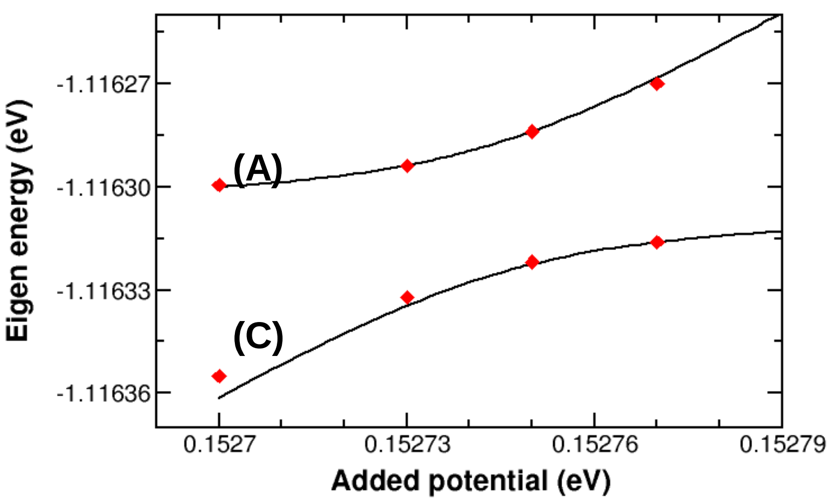
$$E_f = E(N) - [\epsilon_h(Fc) + \lambda_{Fc}]$$

Electronic state coupling and charge transfer rate





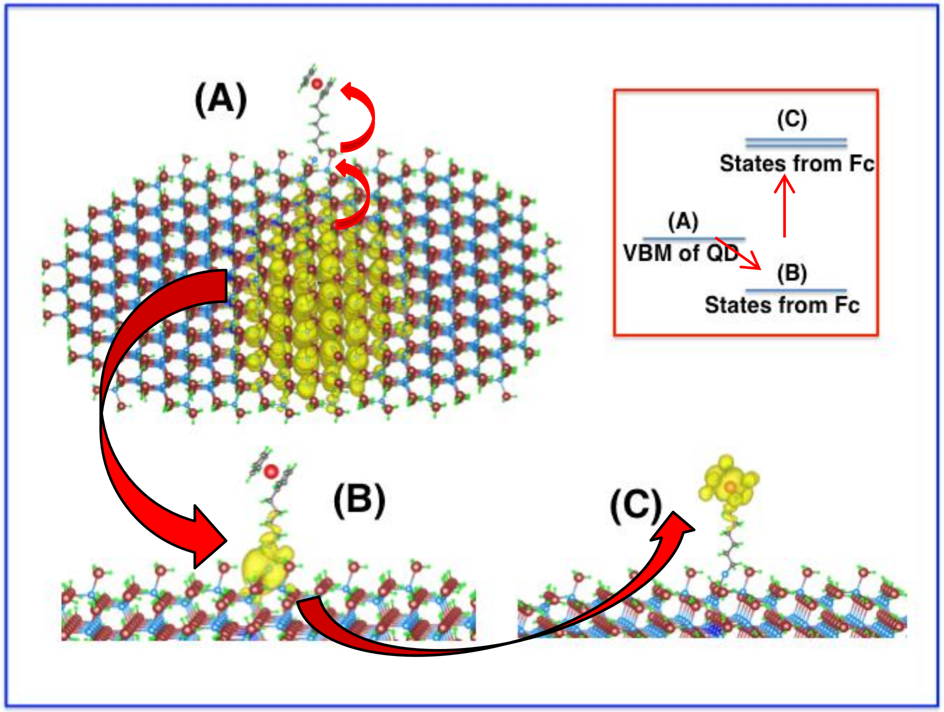
Experimental rate: 1/141 ps – 1/610 ps

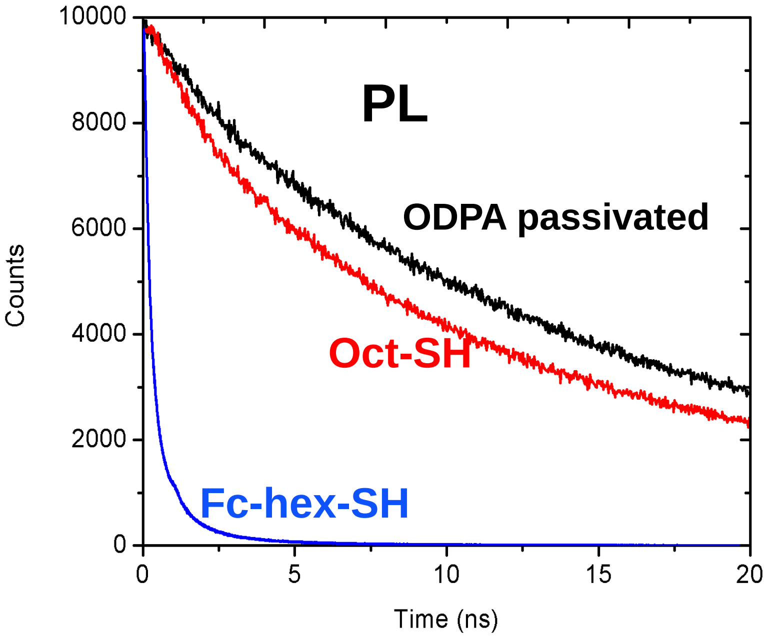


$$Rate = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k T \hbar}} \exp[-(\lambda + \varepsilon_a - \varepsilon_b)^2 / 4\lambda k T]$$

Calculated rate = 1/ 388 ps

Could there be intermediate step?

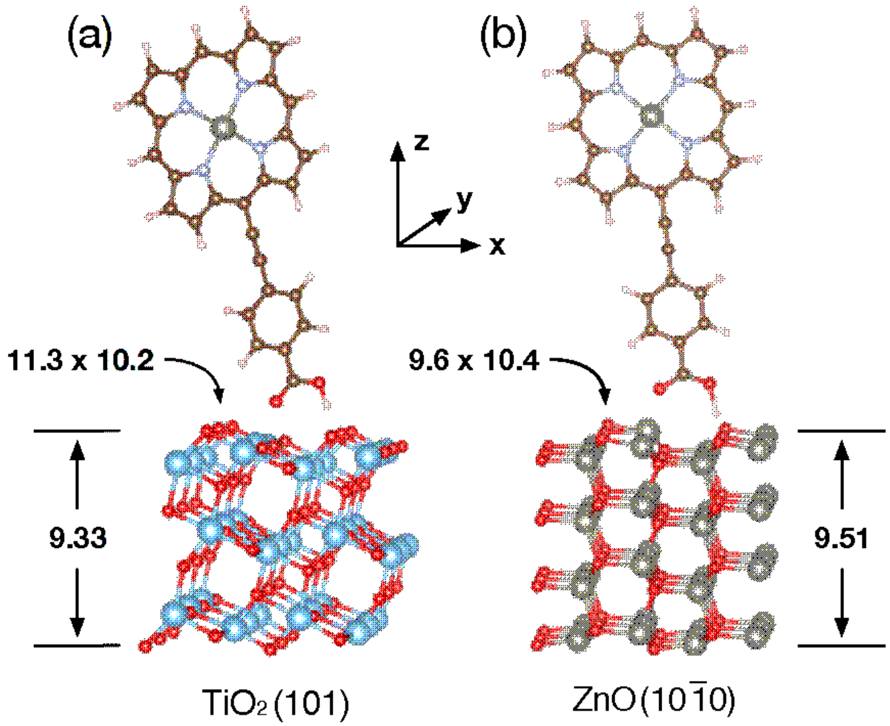




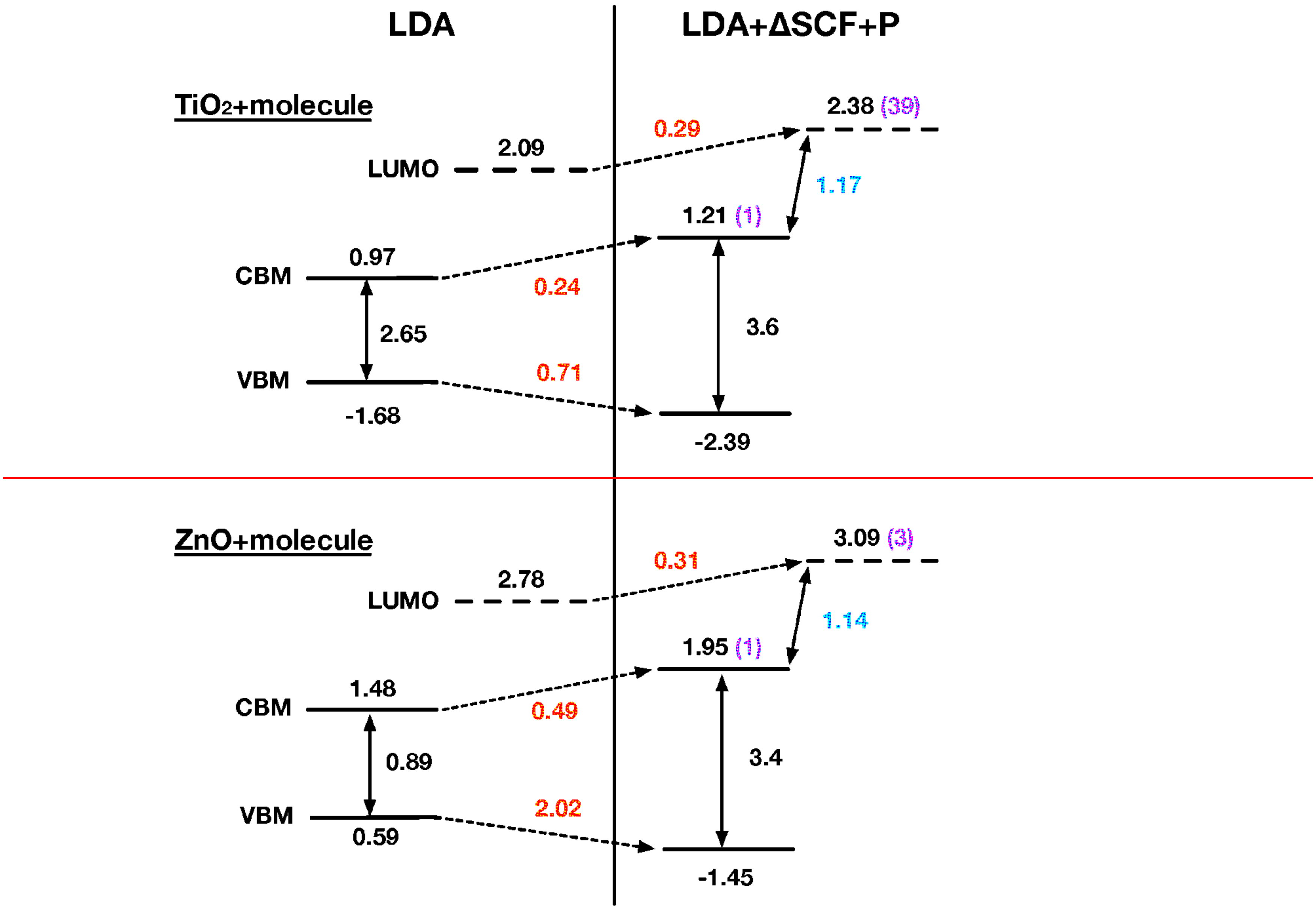
- From the experiment (ODPA to Oct-SH), we know there should be no surface trap state with energy higher than (A).
- For trap state with energy lower than (A), (A)-(B) has a population equilibrium, population on (B) is rather small
- The intermediate state channel is not efficient

Dye sensitized solar cell: Why TiO2 is better

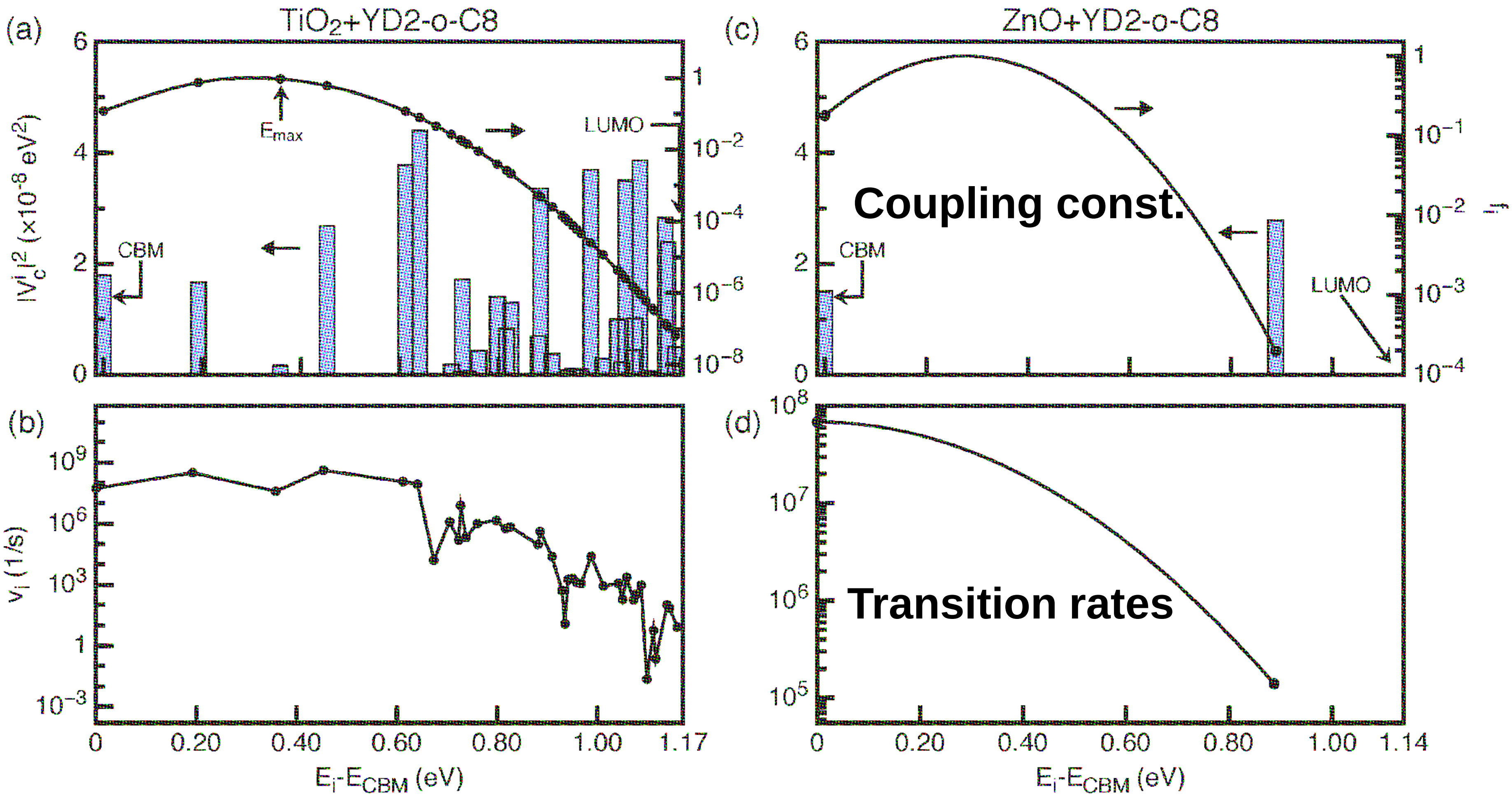
- ZnO has much higher electron mobility
- The band gap and alignments for ZnO, TiO2 are similar
- Like to replace TiO2 with ZnO
- But experimentally, they found TiO2 is much better



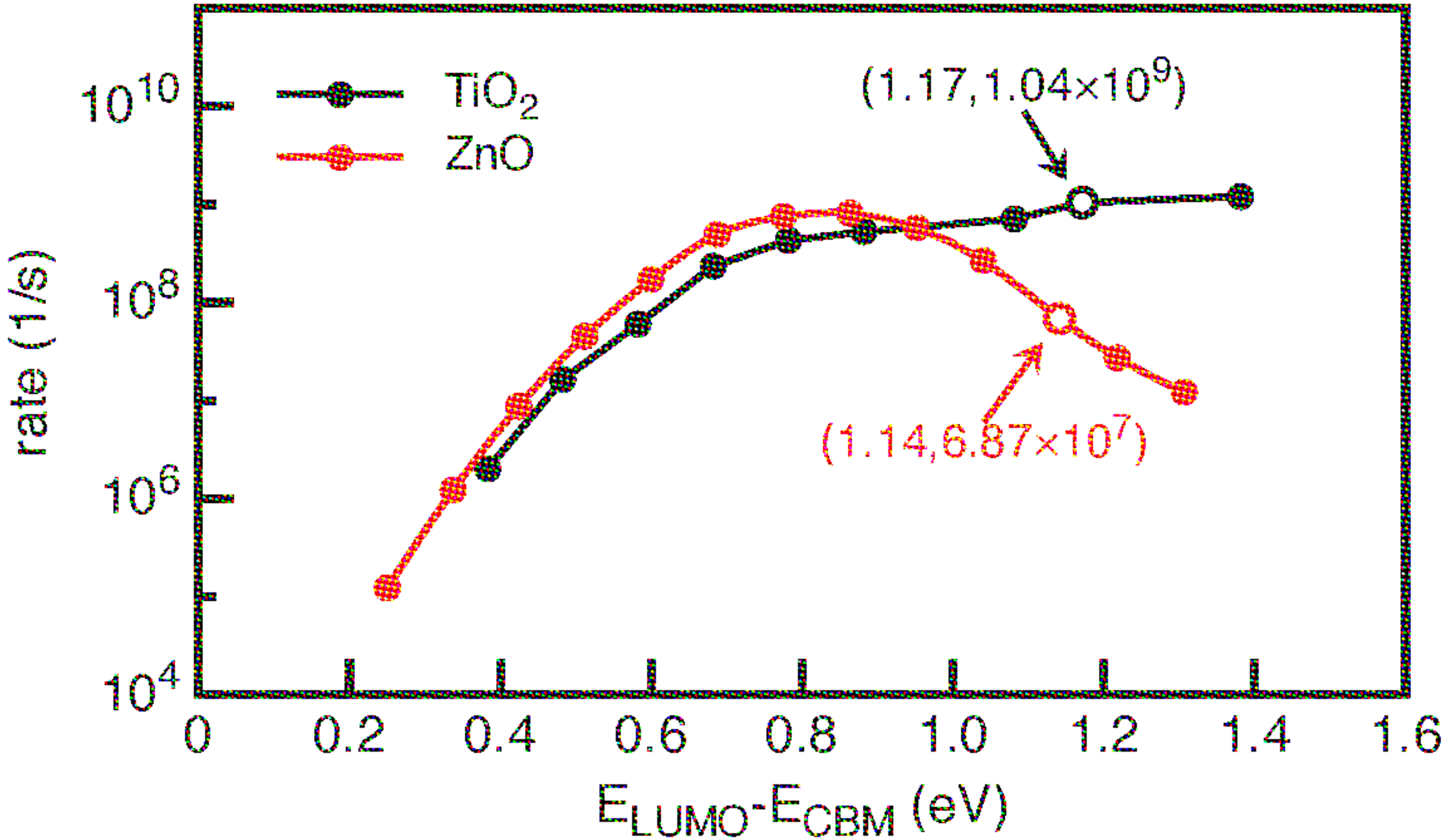
Eigen energy correction from LDA results



The comparison between TiO2 and ZnO



The charge transfer rates



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The formalism (should use static coupling formalism)

$$W = \sum_k \frac{|C_{sl}^k|^2 \omega_k (2\pi)^{1/2}}{2\hbar D} [(\coth y_k + 1)$$
$$\times \exp(-\frac{(\Delta E_{sl} - \hbar\omega_k - E_M)^2}{\omega_k D^2 \hbar^2}) + (\coth y_k - 1)$$
$$\times \exp(-\frac{(\Delta E_{sl} + \hbar\omega_k - E_M)^2}{\omega_k D^2 \hbar^2})] \quad (2)$$

Freed and Jortner, J. Chem. Phys. 50, 2916 (1969).

ω_k : phonon frequency for mode k, $y_k = \beta\hbar\omega_k / 2$

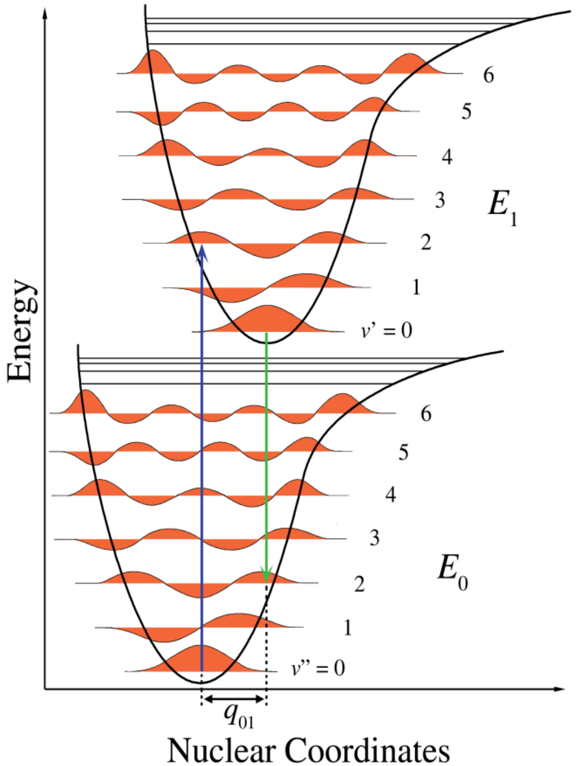
ΔE_{sl} : difference between states s and l

$$C_{sl}^k = \left\langle \psi_s \left| \frac{\partial H}{\partial \mu_k} \right| \psi_l \right\rangle$$ **Electron-phonon coupling constant**

E_M : the reorganization energy

$$D^2 = \sum_j \omega_j^2 \Delta_j^2 (\bar{n}_j + 1/2) \quad \Delta_j = \left(\frac{M_j \omega_j}{\hbar} \right)^{1/2} (Q_j^s - Q_j^l)$$

D^2 is like the reorganization energy E_M (λ)

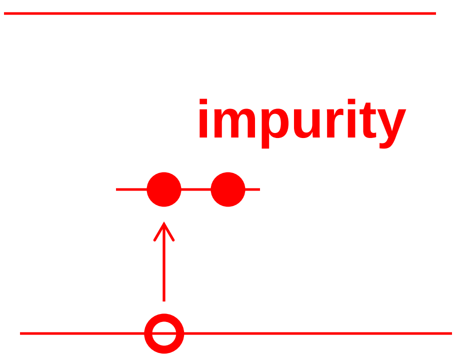


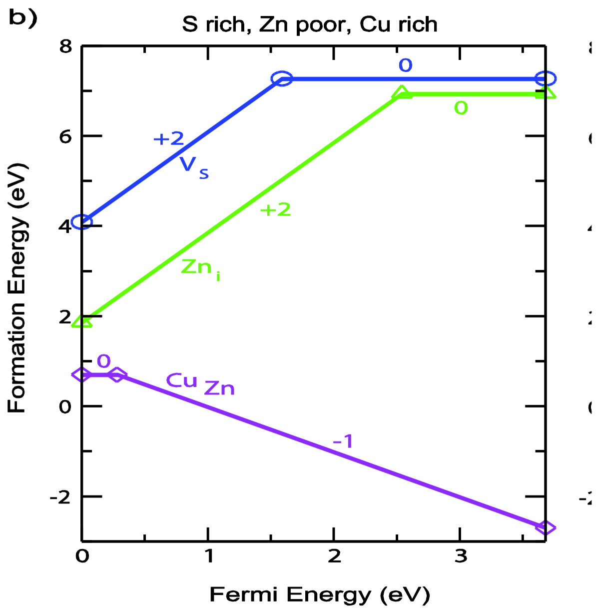
Deep state decay: what we need to calculate?

(1) **Electronic state energies: Using conventional deep state calculation methods (E(N+1)-E(N)).**

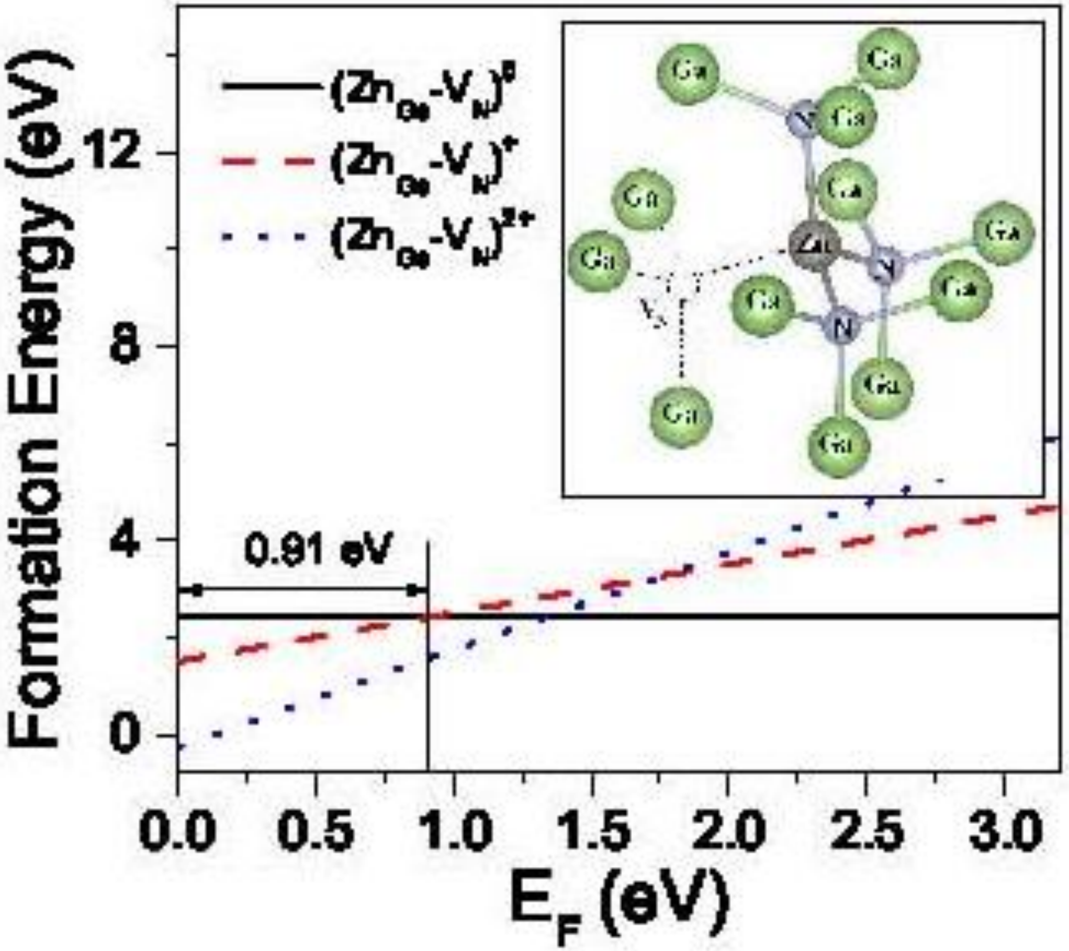
(2) **Phonon frequencies and modes: We will use an approximate method to calculate the dynamic matrix**

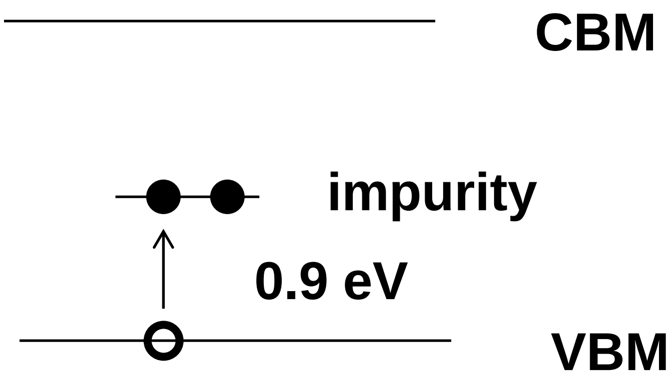
(3) **Electron-phonon coupling constants: We will introduce a new variational algorithm**

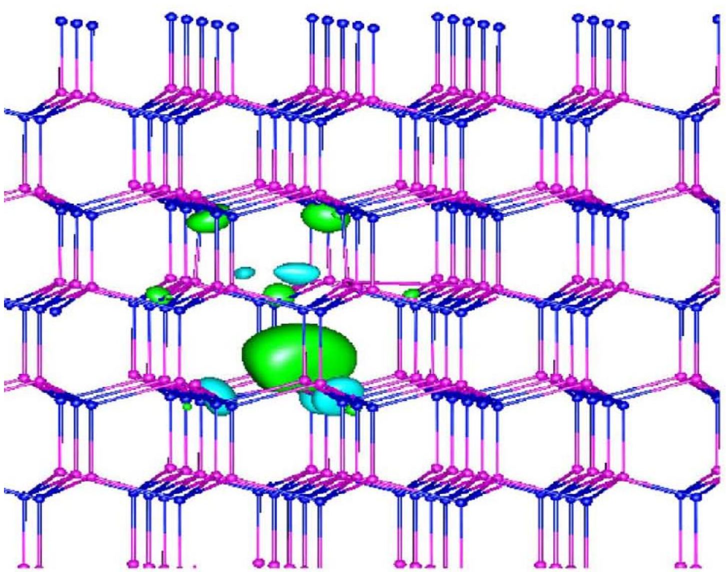




Zn-V_N center in GaN (n-type) for hole trapping





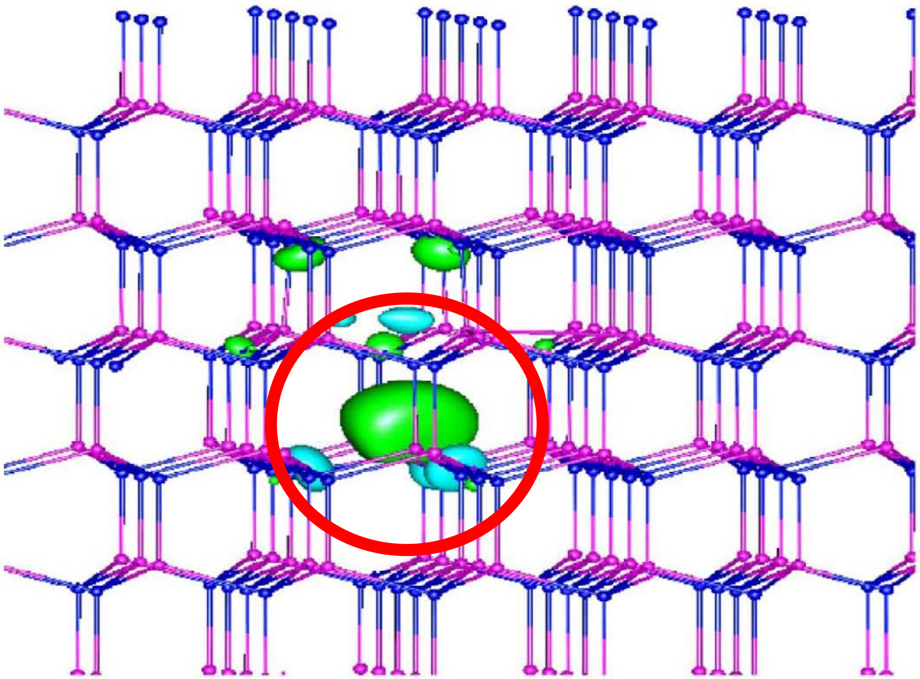


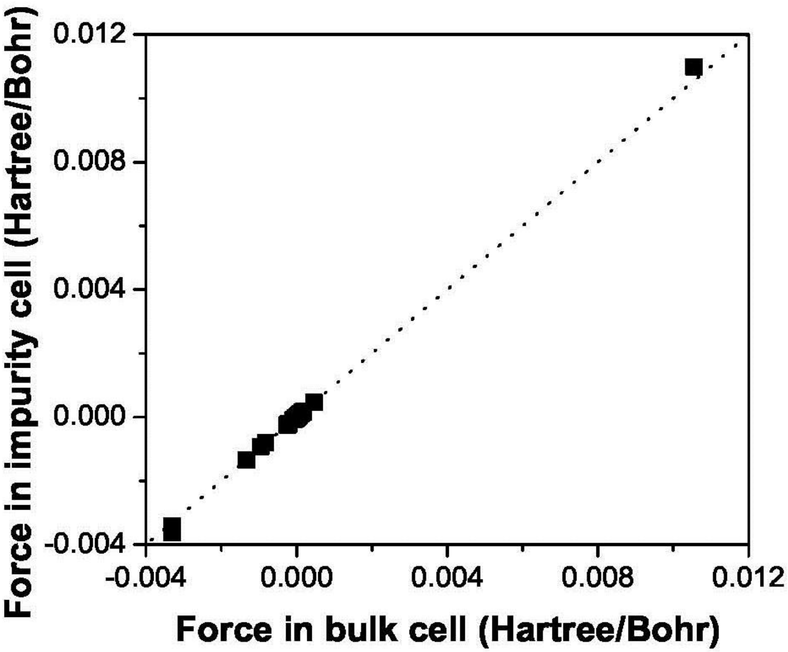
299 atom supercell

Approximated Hessian matrix for phonon mode

$$\sum_{R'} M(R,R')\mu_k(R') = \omega_k^2 \mu_k(R)$$

$$M(R,R') = \frac{1}{\sqrt{M_R M_{R'}}}\frac{\partial^2 E}{\partial R \partial R'} = \frac{1}{\sqrt{M_R M_{R'}}}\frac{\partial F_R(R')}{\partial R'}$$





Electron-phonon calculations

$$C_{sl}^{k} = \langle \psi_s | \frac{\partial H}{\partial \mu_k} | \psi_l \rangle$$

Ψ_s, ψ_l are already known, but need hundreds of SCF calc. to get $\delta H/\delta\mu_k$.

New algorithm: one SCF calculation to get all C^k_{sl}:

$$\rho(r) = \sum_{i \in occ} |\psi_i|^2 + \lambda \psi_l \psi_k (\, fixed\,)$$

Then normal SCF calculation to get the KS wave functions, and Feynman-Hellman method to calculate the atomic forces F_R

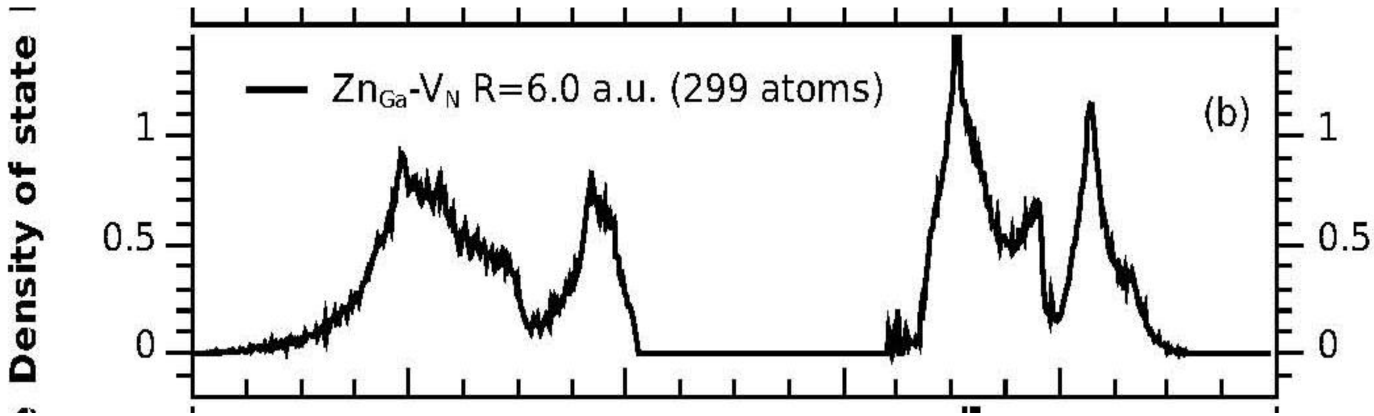
Then one can prove (using variational principle):

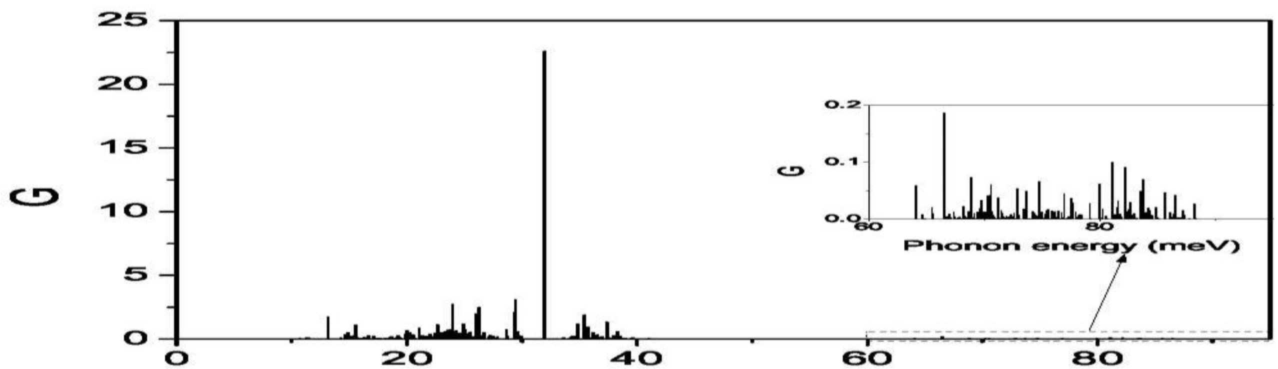
$$F_R = \langle \psi_l | \frac{\partial H}{\partial R} | \psi_k \rangle$$

Then, F_R, together with phonon mode $\mu_k(R)$ can be used to construct C^k_{sl}.

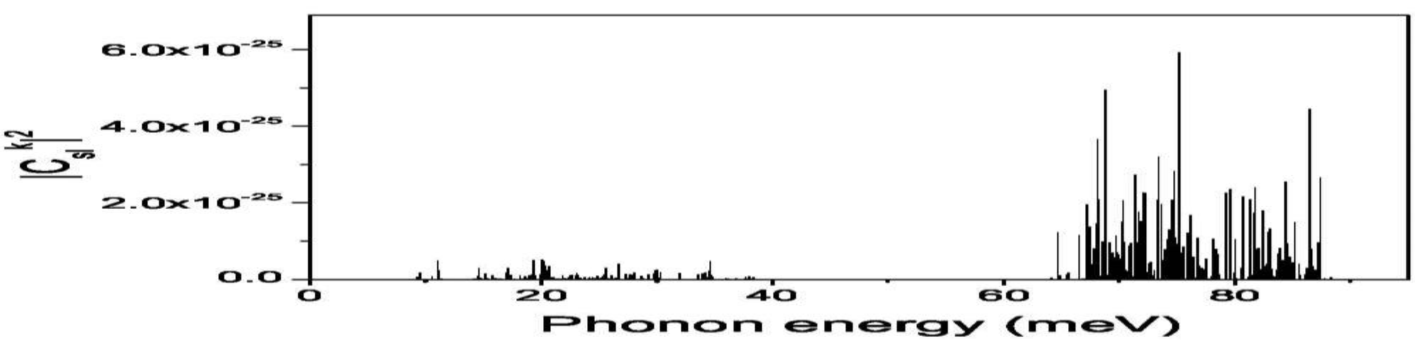
Similar formalism also works for hybrid functional

The roles of different phonon modes





Passivation modes (multiple phonon emission to satisfy energy conservation)



Stimulation modes (large electron-phonon coupling constants)

Office of Science
U.S. DEPARTMENT OF ENERGY

The results using different formalisms

BERKELEY LAB

	Exp	Static	Adiabatic	Marcus theory	Quantum CT rate	1D quantum formula
GaP:Zn_{Ga}-O_P	$(4^{+2}_{-1}) \times 10^{-8}$	4.30×10^{-8}	3.32×10^{-10}	7.32×10^{-8}	6.44×10^{-8}	1.68×10^{-10}
GaN:Zn_{Ga}-V_N	3.0×10^{-7}	1.46×10^{-7}	5.57×10^{-10}	1.18×10^{-8}	1.21×10^{-8}	1.5×10^{-9}

Outline

- A multiscale calc. of single phonon assisted hopping (N. Vukmirovic)
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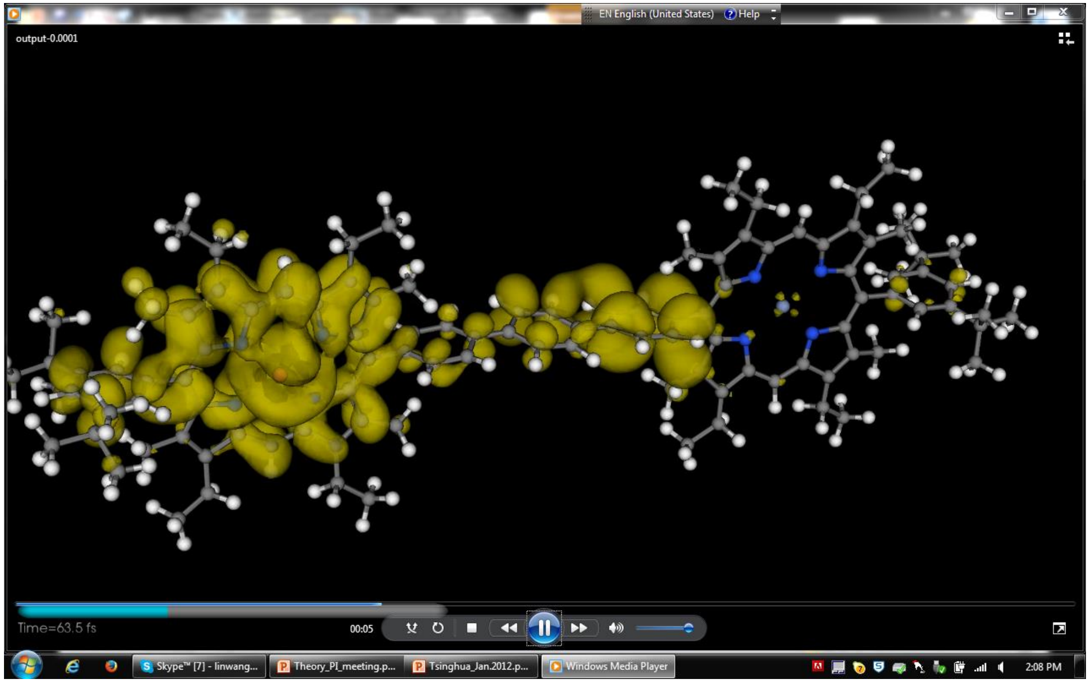
- Real-time TDDFT calculations (Z. Wang, J. Ma)
- GPU speed up for electronic structure calculations (W.L. Jia)

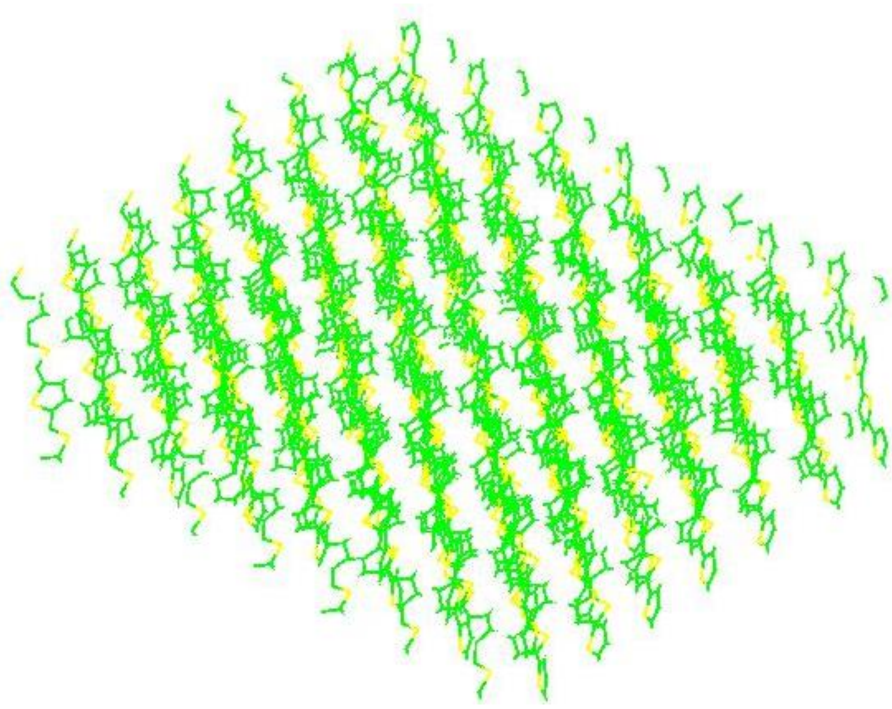
Direct wave function time evolution

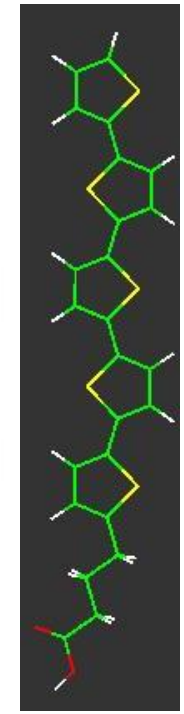


- Time dependent Schrodinger's Eq. for electron wave function
- Newton's law for nuclear movement

One monolayer of D5TBA on a substrate

Herringbone structure





❖ The VFF structure agrees with experiments (after some fitting on VFF)

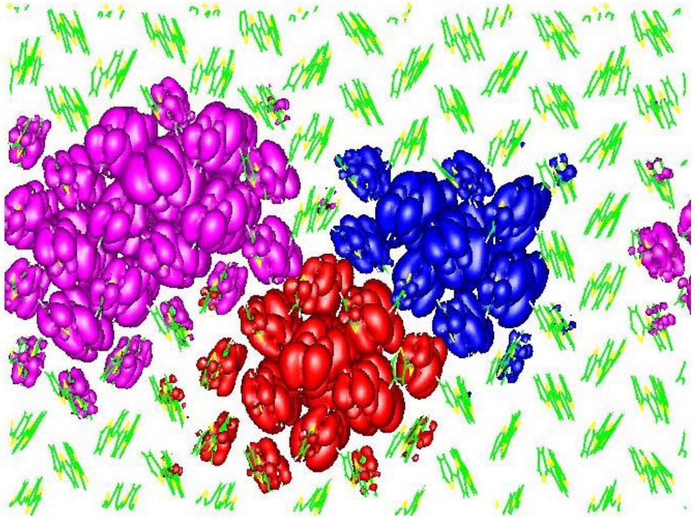
❖ Experiments are setting up to measure the in-plane mobility (M. Salmeron)

❖ There are some fundamental questions for carrier dynamics

(Hendriksen, et.al, Nano Lett. 11, 4107 (2011))

Questions for the carrier dynamics

- ❖ Should we use phonon assisted state hopping to describe carrier mobility?
- ❖ Should we use Marcus theory (state crossing) ?
- ❖ Maybe the states will move with time (coherent transport).



Method to use:

A time-domain simulation can capture all these effects.

(1) $\ddot{R}(t) = mF$

(2) $i\frac{\partial}{\partial t}\psi(t) = H[R(t)]\psi(t)$

(3) some state collapses (dephasing)

(Ren, et.al, P.R.B, 87, 205117 (2013)

Techniques and approximations

(1) Treat nuclei molecular dynamics (MD) with classical force field using LAMMPS

(2) Some special way to treat surface hopping(Tully algorithm)

(3) Obtain H[R(t)] using charge patching method (CPM)

(4) Solve the adiabatic eigen states $\phi_i(t)$ using overlapping fragment method (OFM).

Implications:

(1) Decouple the nuclei MD with electron dynamics, might have consequence for polaron effects (will be added later).

(2) Decoherence might be important (different algorithm will be tested later)

Solving the time dependent Schrodinger's equation

$$i\frac{\partial}{\partial t}\psi(t) = H[R(t)]\psi(t)$$

$$H[R(t)]\phi_i(t) = \varepsilon_i(t)\phi_i(t)$$

$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij}$$

$$V_{ij} = \left[\left\langle \phi_i(t) \middle| \phi_j(t+\Delta t)\right\rangle - \delta_{ij}\right] / \Delta t$$

Task: to calculate ϕ_i for many snapshots (Δt);
R(t) is already known from force field MD

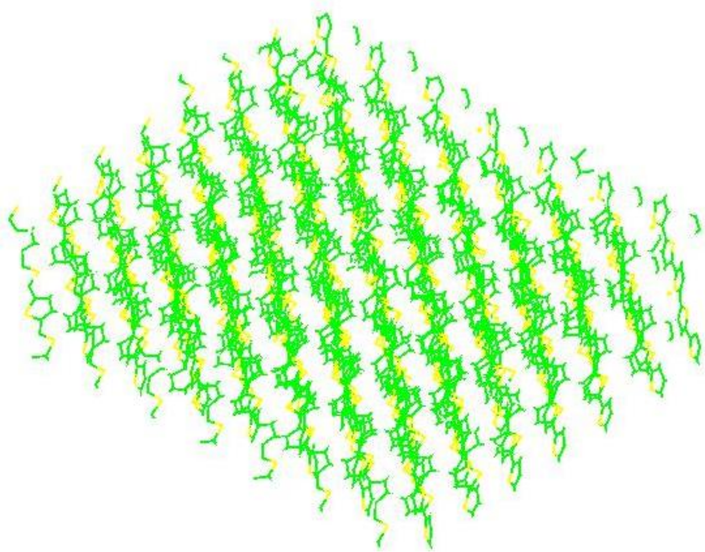
Calculating the electronic states using fragment basis

- Generate the basis set on each trimer of the thiophene rings

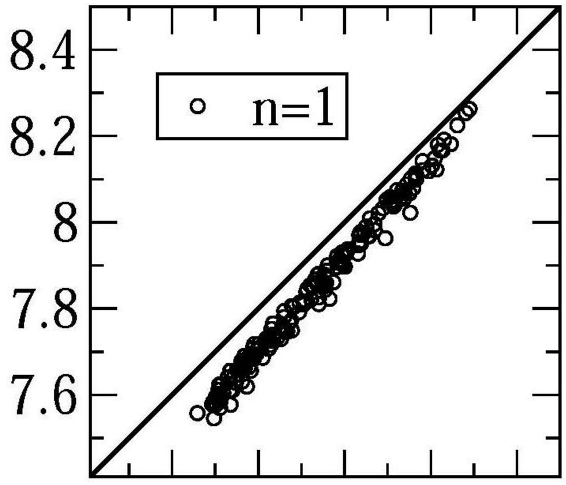
- The trimers are overlapping with each others.

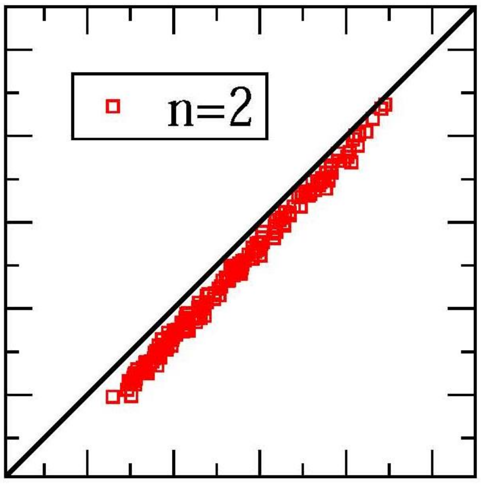
- The number of basis set equal to the number of thiophene rings (or by x2, x3)

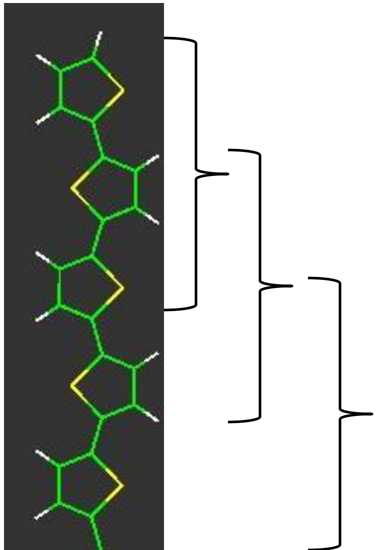
- But each trimer fragments cut from the system have to be calculated.



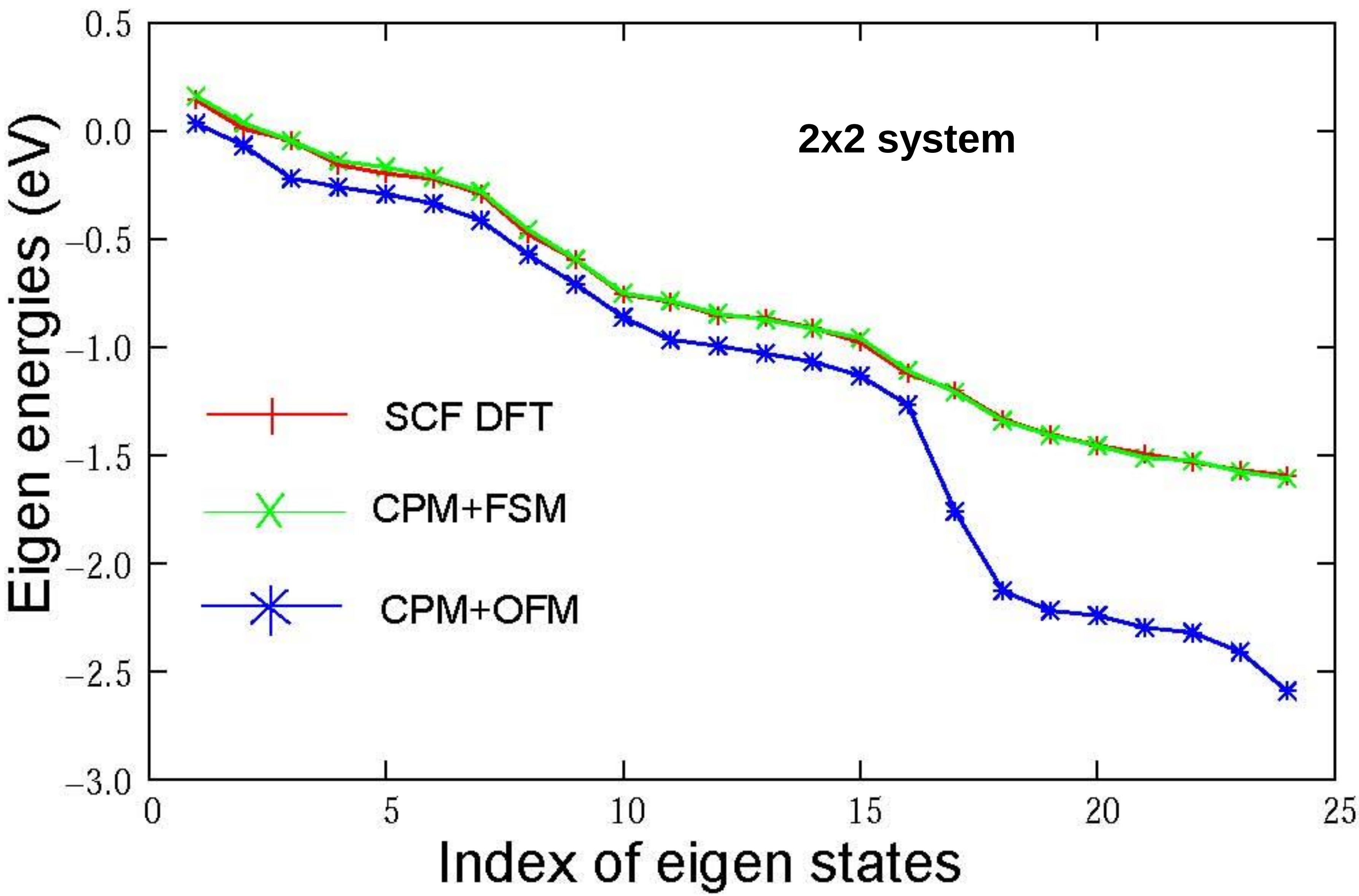
(Vukmirovic, Wang, J. Chem. Phys 134, 094119 (2011))







The quality of the charge patching method and OFM

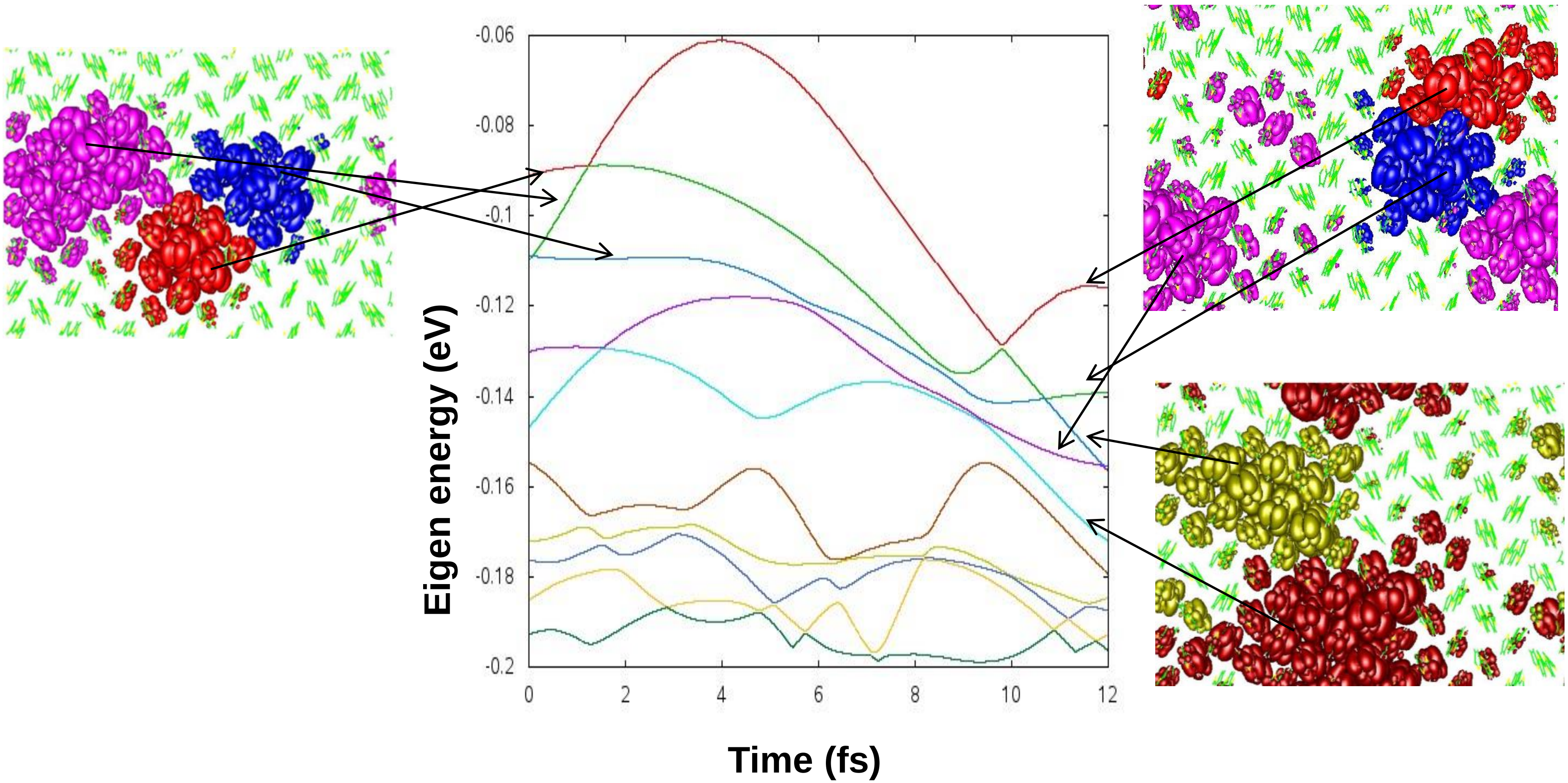


The computation: massive parallelization

- One OFM takes 2352 CPU
- 2352 divided into 294 groups with 8 CPU in one group
- One group calculates one fragment
- One OFM job (2353 CPU) calculate 25 snapshots (0.5 fs apart), one after another
- 22 OFM jobs (51,744 CPU) calculate simultaneously on Jaguarpf
- 1650 snapshots (825 fs) take about 2 hours.

One job = 12 year on laptop!

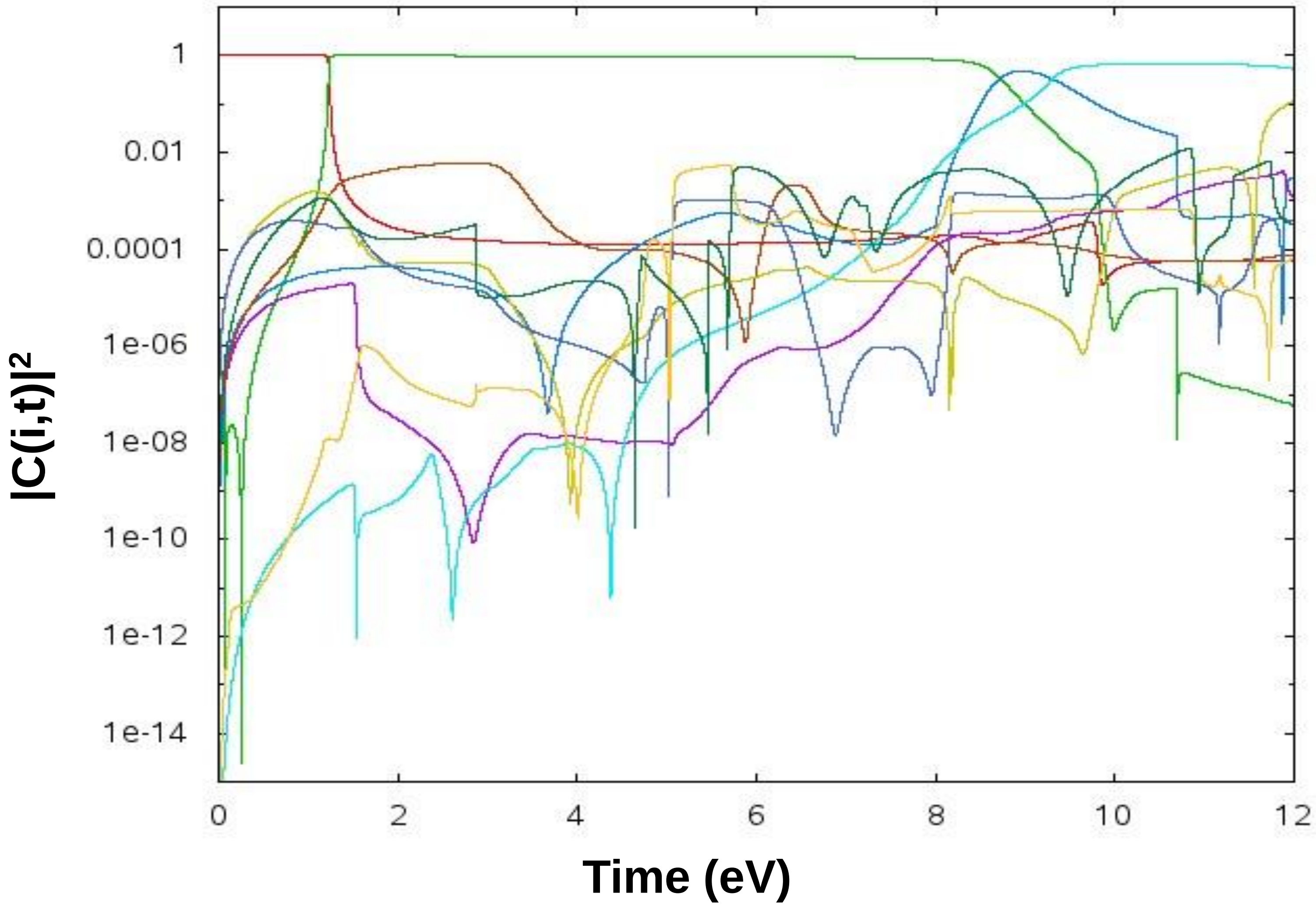
Eigen energies and eigen states



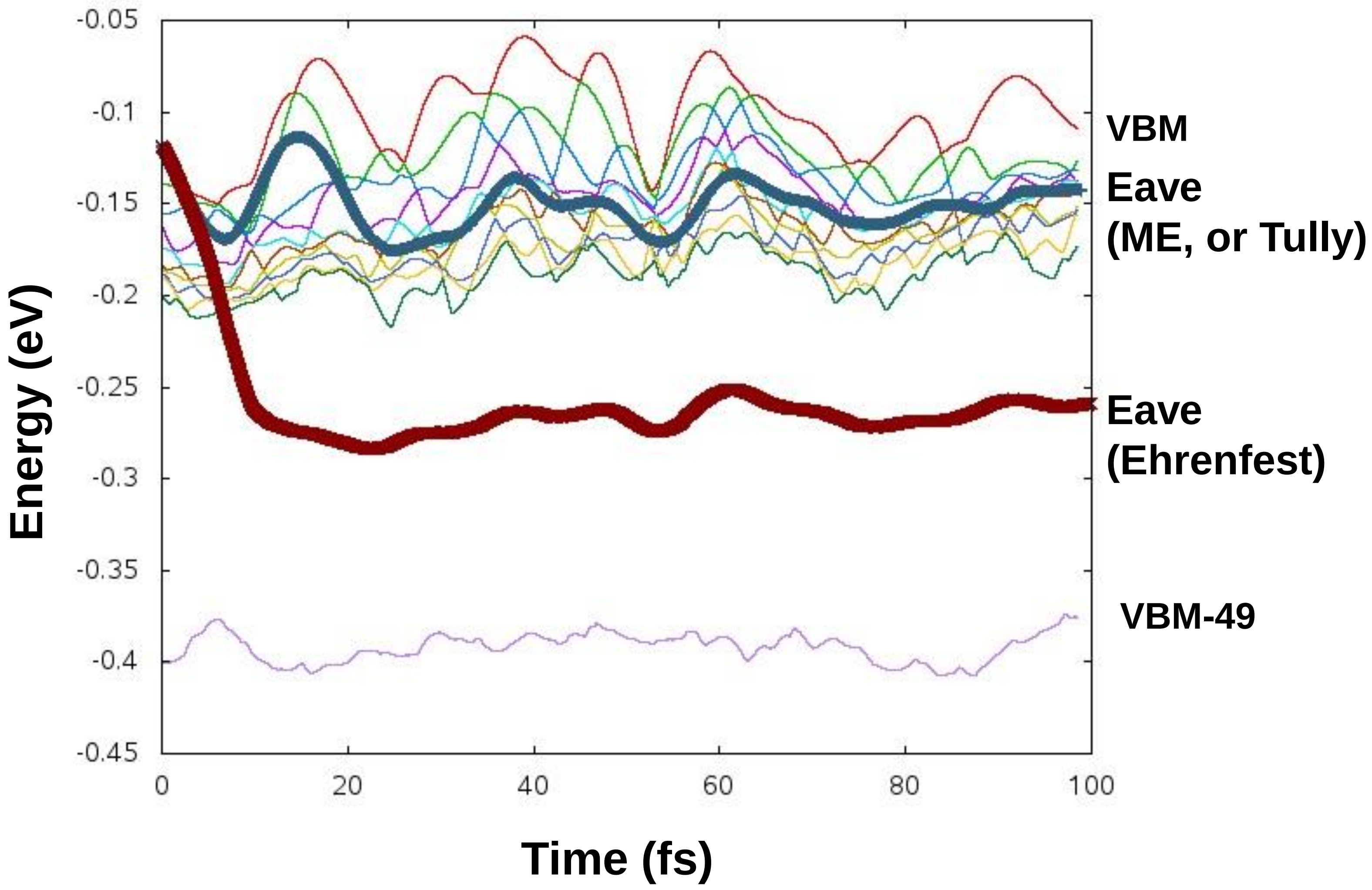
- ❖ **One can trace the eigen states**
- ❖ **The state location might not change much, but its energy changes a lot (0.06 eV)**

The coefficient $|C|^2$

$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$



New results


-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
-0.4
-0.45
0
20
40
60
80
100
Energy (eV)
Time (fs)
VBM
Eave
(ME, or Tully)
Eave
(Ehrenfest)
VBM-49

What is wrong?

- ❖ **The Boltzmann distribution is not maintained, electron system is over heated.**

- ❖ **Nuclei movement is treated classically, no zero phonon movement, which is essential for Boltzmann distribution**

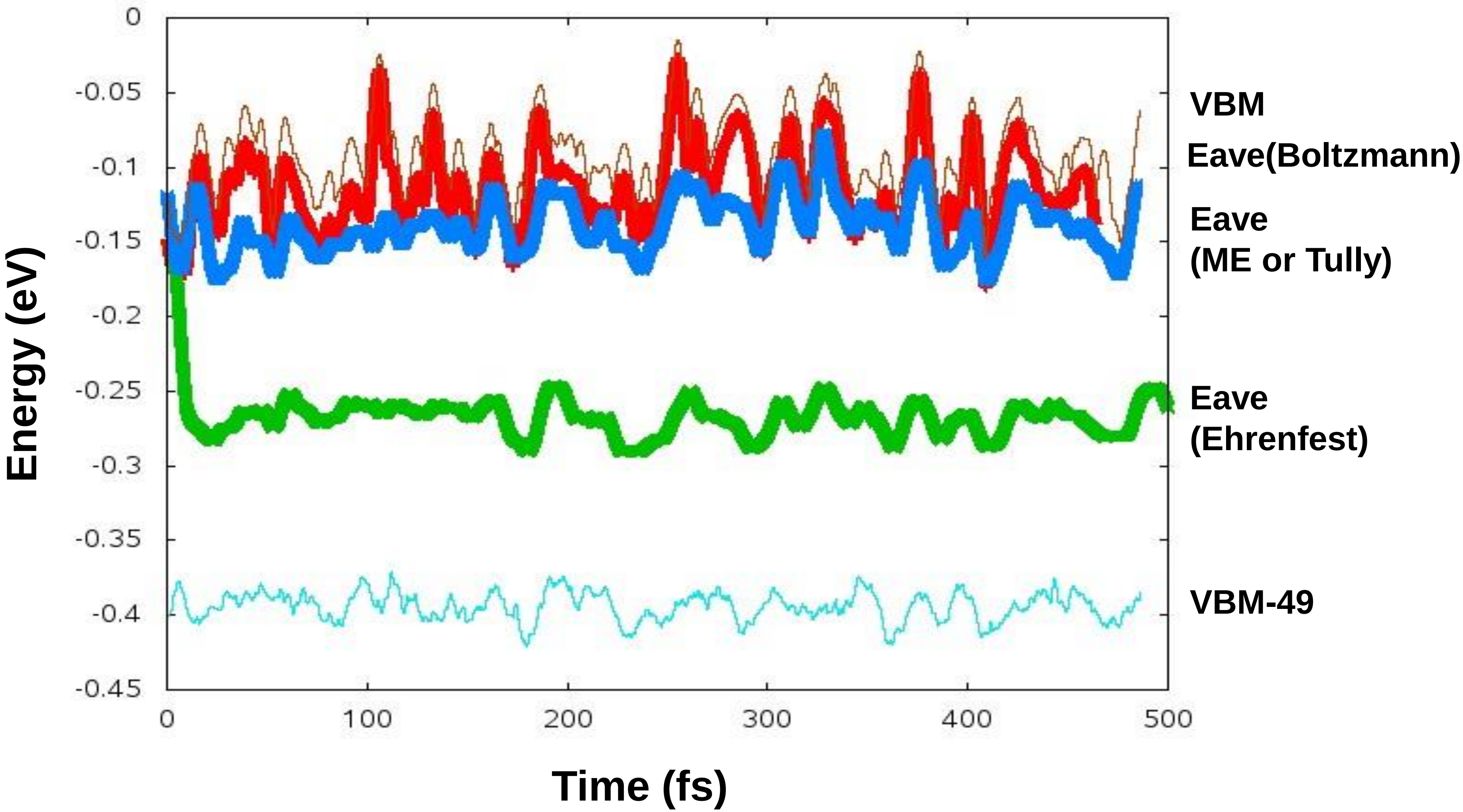
- ❖ **An empirical fix**

$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij} \times \begin{cases} \exp(-|\varepsilon_i(t)-\varepsilon_j(t)|/kT) & \text{If } \varepsilon_i<\varepsilon_j \text{ and i loses weight or } \varepsilon_i>\varepsilon_j \text{ and i gains weight} \\ 1 & \end{cases}$$

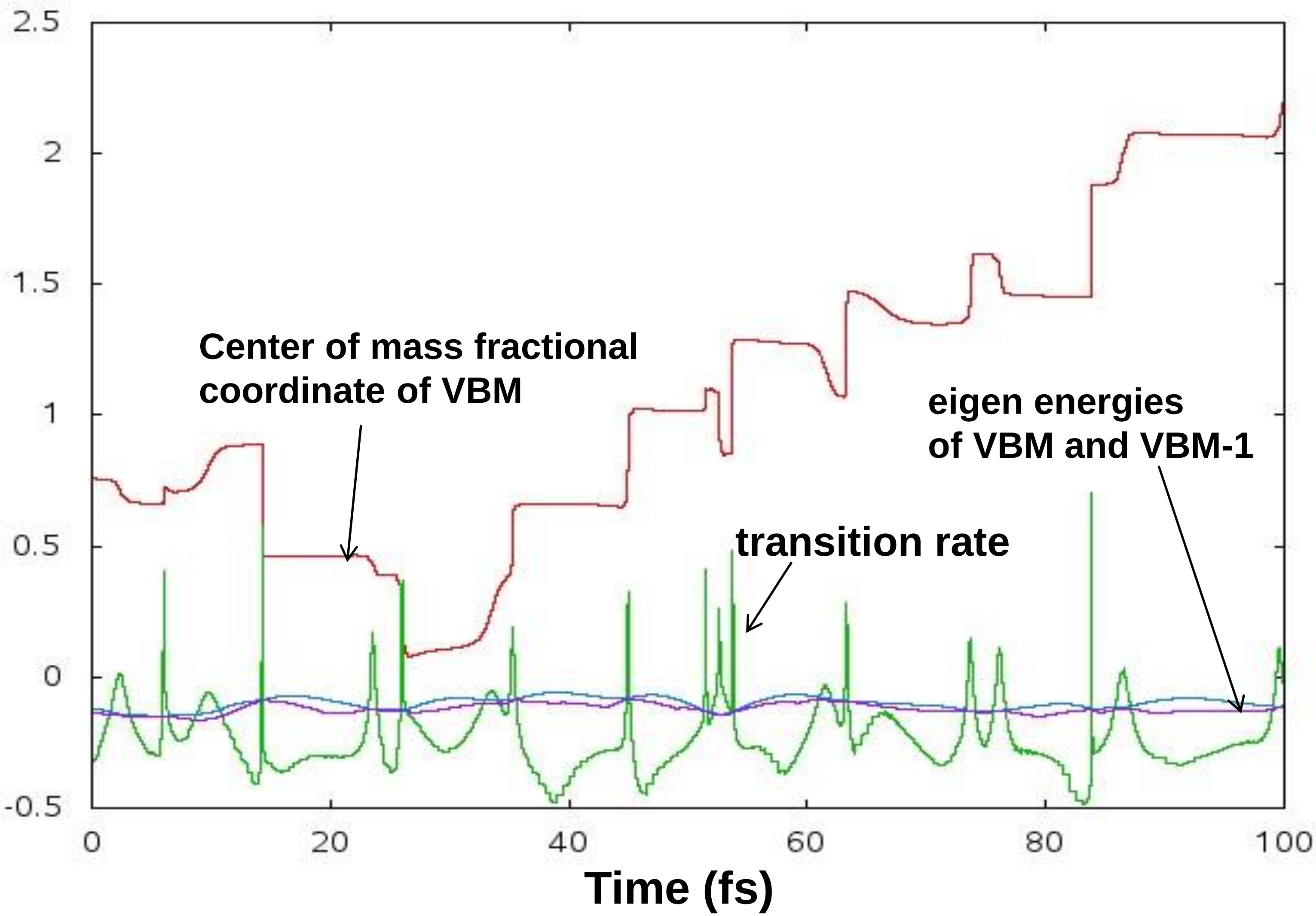
If $\varepsilon_i<\varepsilon_j$ and i loses weight
or $\varepsilon_i>\varepsilon_j$ and i gains weight

New results

The system is never in equilibrium according to Boltzmann distrib.

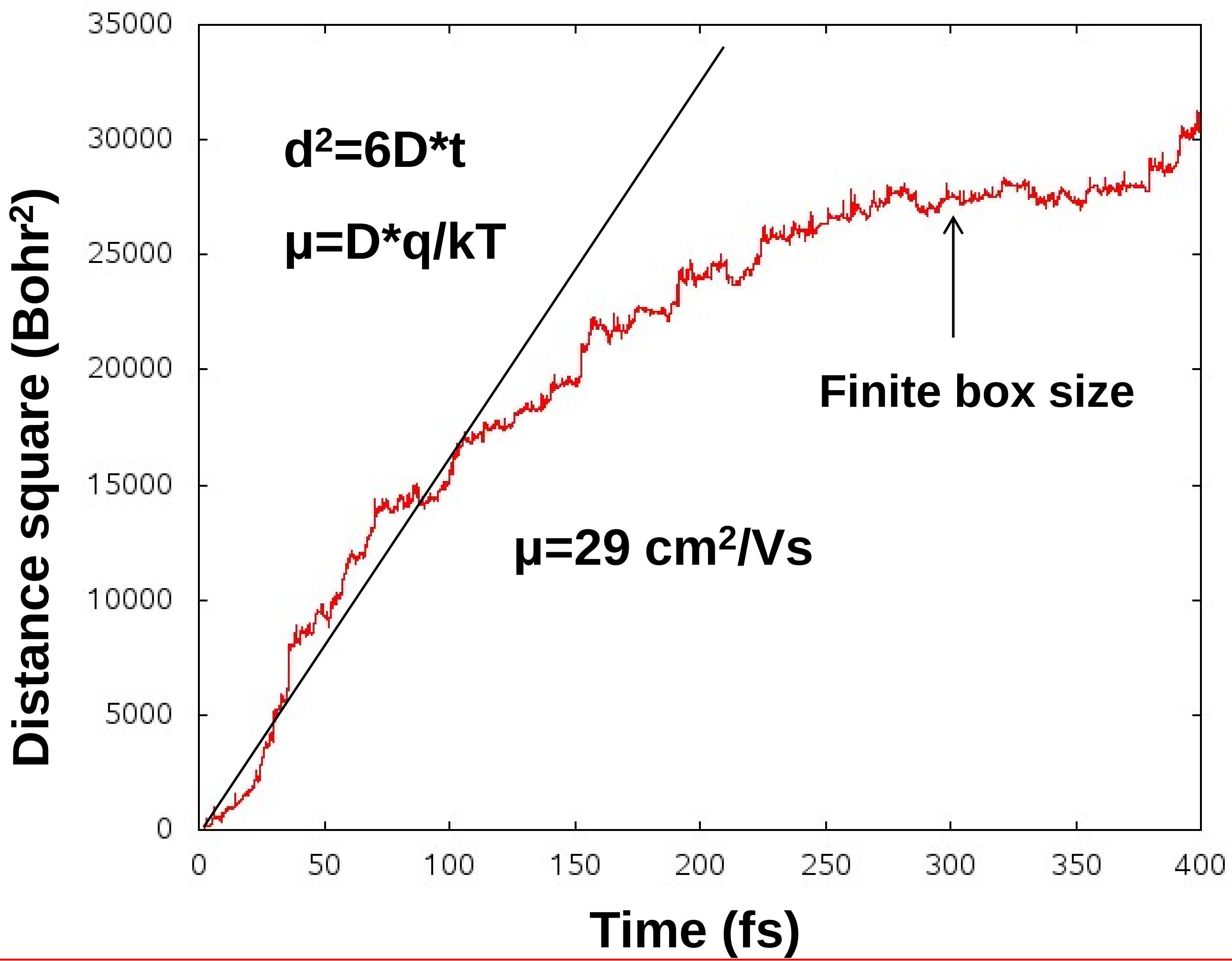


The eigen state positions



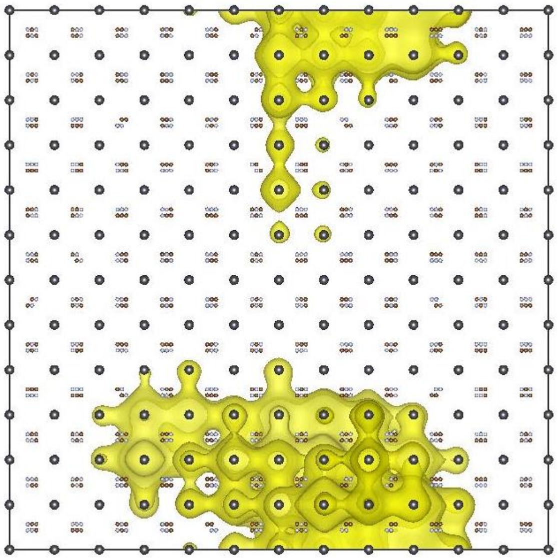
- The drifting of eigen state positions are rather slow
- The diffusion is caused by state energy crossing (under thermo fluctuation).

Diffusion distance and mobility

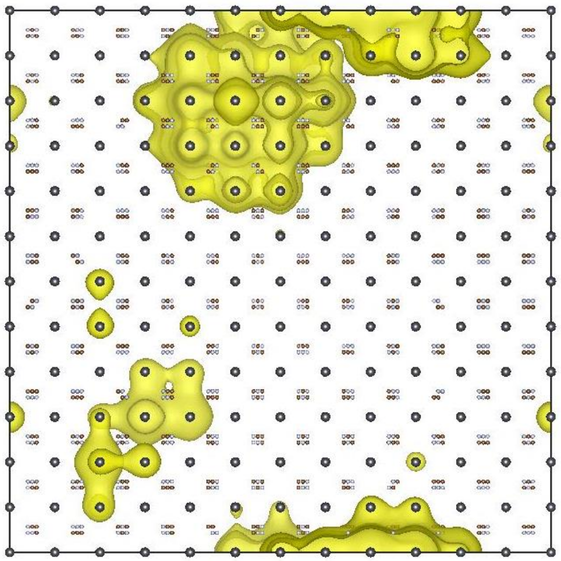


If we turn off any φ_i to φ_j transition with $|\varepsilon_i-\varepsilon_j|>$ 5meV, the diffusion constant does not change:
The diffusion is not due to single phonon absorption/emission

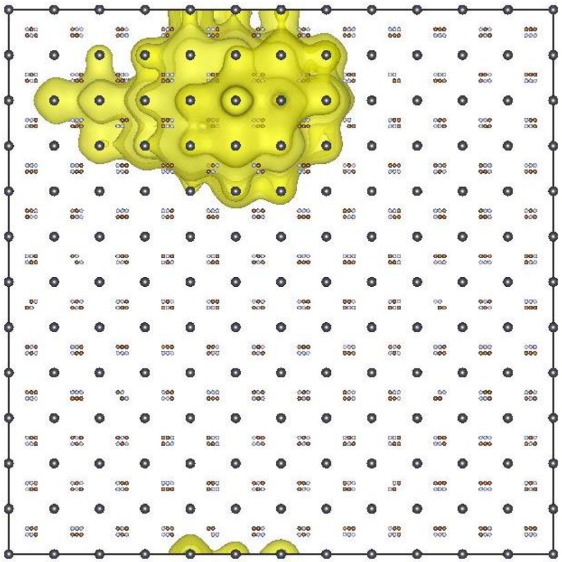
Nonadiabatic MD for carrier diffusion in $MAPbI_3$



t = 0



t = 50000 a.u.



t = 50000 a.u.
Adiabatic state

1 flip per molecule per ps

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Real-time TDDFT method (rt-TDDFT)

Rt-TDDFT can be used to study many phenomena

- System response to an arbitrary V(r,t) perturbation
- Nonlinear response coefficients
- Ultra-fast dynamics (carrier cooling and charge injection)
- Ion-collision
- Carrier transports

We will implement rt-TDDFT as Ehrenfest dynamics

- time dependent Schrodinger's eq for electron dynamics
- Newton's law for nuclear dynamics

$$E_{tot} = \sum_R \frac{1}{2} M_R \dot{R}^2 + E_{DFT}[\psi_i, R]$$

$$\begin{cases} i \dfrac{\partial \psi_i(t)}{\partial t} = H_{KS}[\rho(t)]\psi_i(t) \\ M_R \ddot{R} = F_R \end{cases}$$

$$\rho(t) = \sum_i \psi_i(t)^2$$

$$F_R = \frac{\partial}{\partial R} E_{DFT}[\psi_i, R]$$

Hellman-Feyman force

Solving the TDDFT on adiabatic basis set

$$i\frac{\partial}{\partial t}\psi(t) = H[R(t)]\psi(t)$$

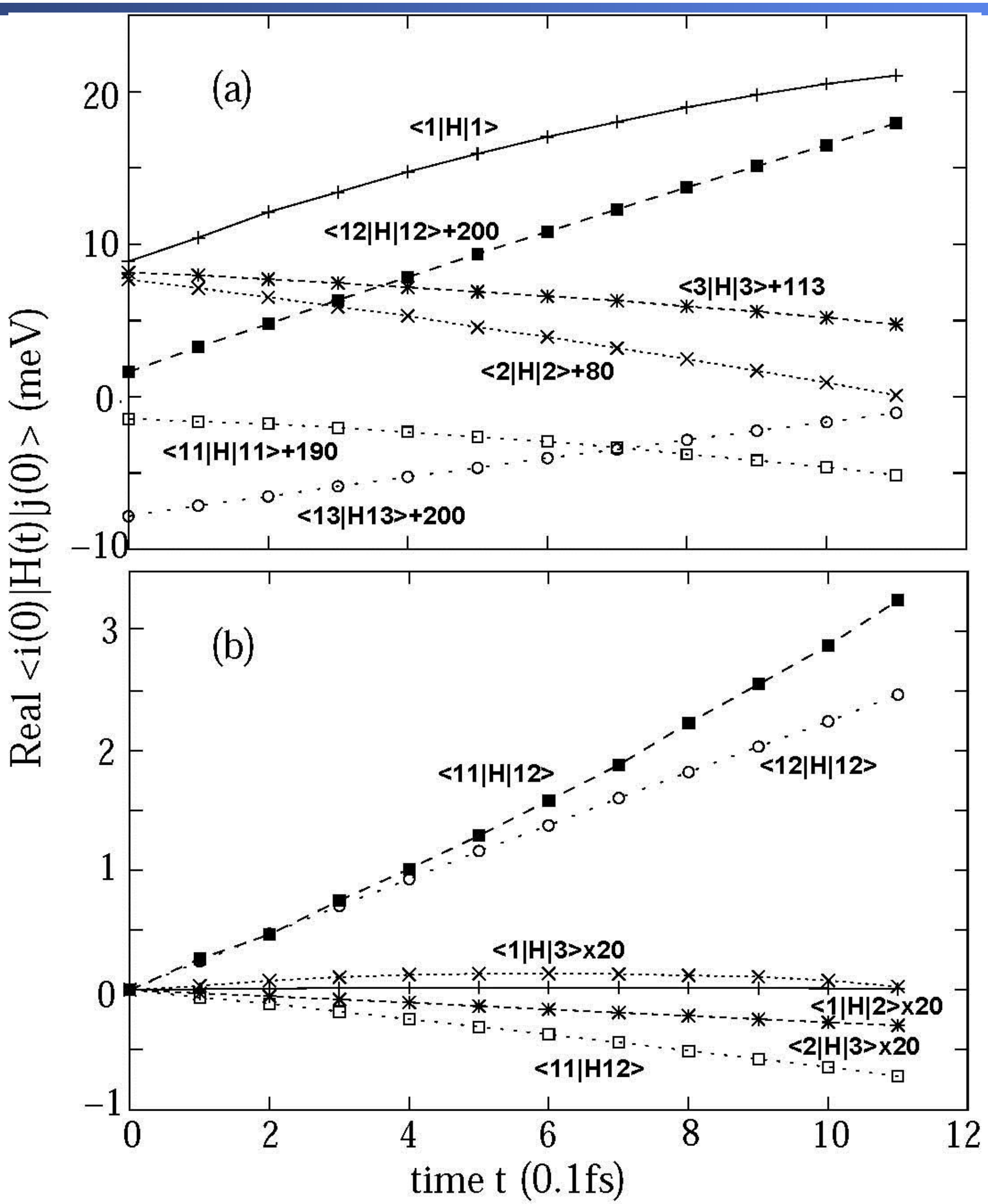
$$\psi(t) = \sum_i C(i,t)\phi_i(t)$$

$$H[R(t)]\phi_i(t) = \varepsilon_i(t)\phi_i(t)$$

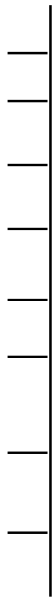
$$\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_j C(j,t)V_{ij}$$

$$V_{ij} = \left[\left\langle \phi_i(t) \middle| \phi_j(t+\delta t)\right\rangle - \delta_{ij}\right] / \delta t$$

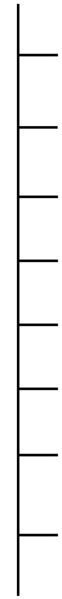
Linearity of ΔH



A further simplification



$$H_{i,i'}(t) = \langle \varphi_i(t_1) | H(t) | \varphi_{i'}(t_1) \rangle = H_{i,i'}(t_1) + (t - t_1)\Delta H_{i,i'}$$



$$\varphi_i(t_1) \qquad\qquad \varphi_i(t_1 + \Delta t)$$

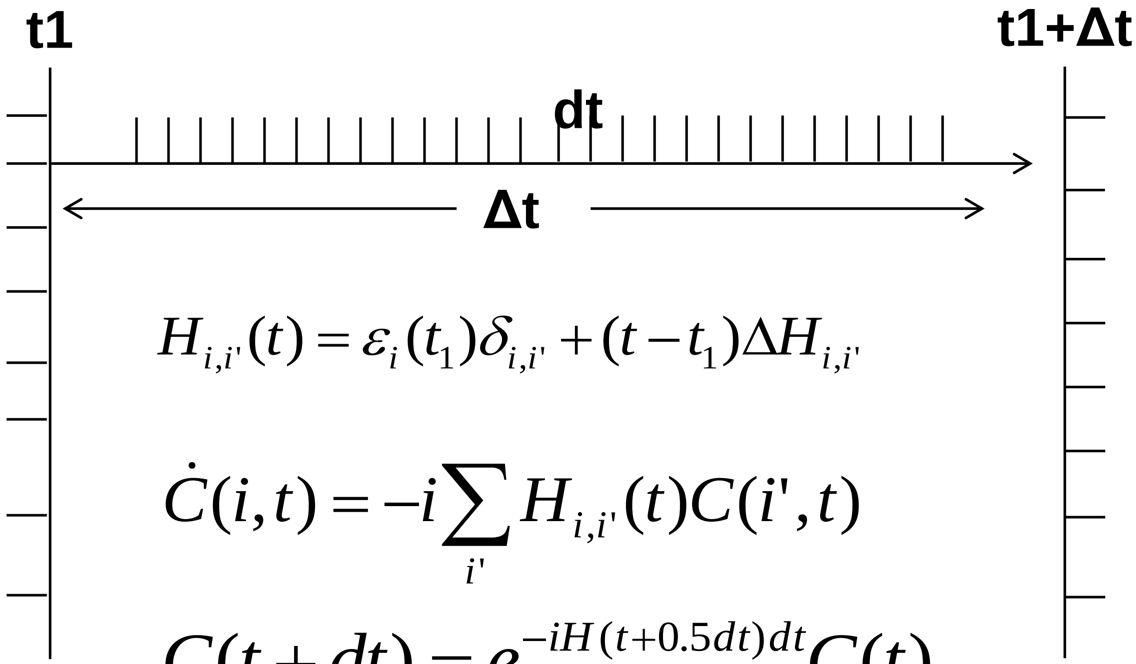
$$\rho(t_1) = \sum_j \psi_j(t_1)^2 \qquad\qquad \rho(t_1 + \Delta t) = \sum_j \psi_j(t_1 + \Delta t)^2$$

Instead of: $\dot{C}(i,t) = -i\varepsilon_i(t)C(i,t) - \sum_{i'} V_{i,i'}(t)C(i',t)$ **V_{ij}(t)can have sharp peak with t**

We do: $\dot{C}(i,t) = i\sum_{i'} H_{i,i'}(t)C(i',t)$ **(no need to diagonalize H every dt)**

Integrate ψ from t_1 to $t_1+\Delta t$

Leapfrog SCF iteration between t1, and t1+Δt



$$H_{i,i'}(t) = \varepsilon_i(t_1)\delta_{i,i'} + (t-t_1)\Delta H_{i,i'}$$

$$\dot{C}(i,t) = -i\sum_{i'} H_{i,i'}(t)C(i',t)$$

$$C(t+dt) = e^{-iH(t+0.5dt)dt}C(t)$$

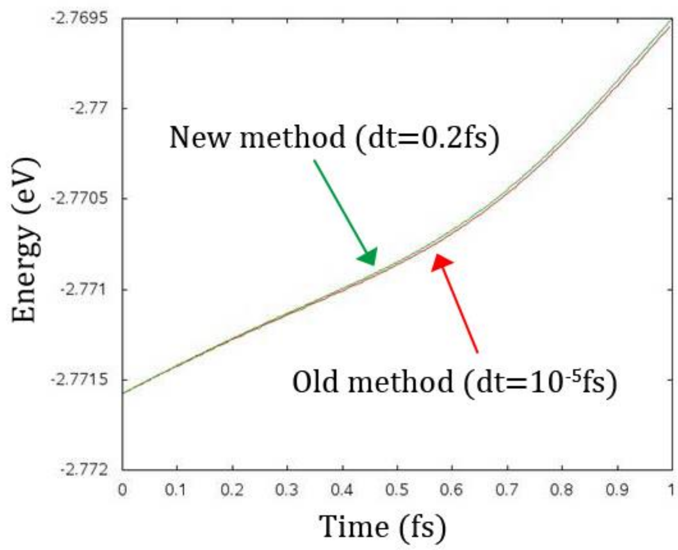
$$= e^{-i0.5\varepsilon_i dt}e^{-i(t+0.5dt-t_1)\Delta H}e^{-i0.5\varepsilon_i dt}C(t)$$

dt → 10^{-4} fs

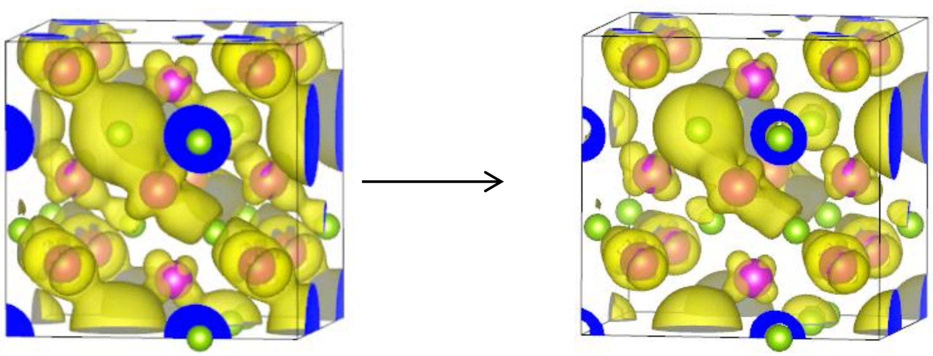
Taylor expansion

Due to the truncation of adiabatic basis (typically 10 eV above CBM), the integration of C does not take time

Comparison: new method and conventional method

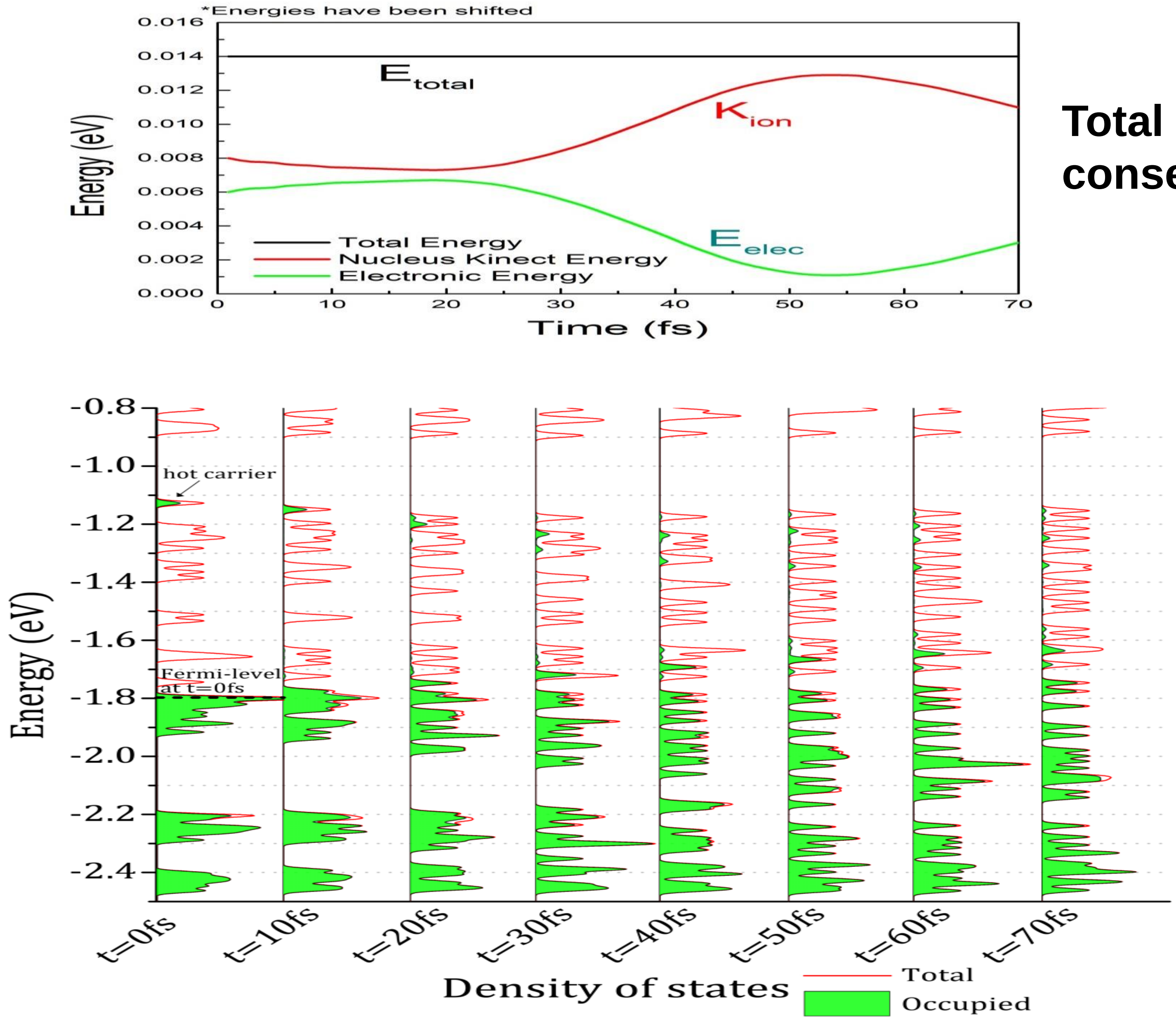


CdSe bulk with random movement



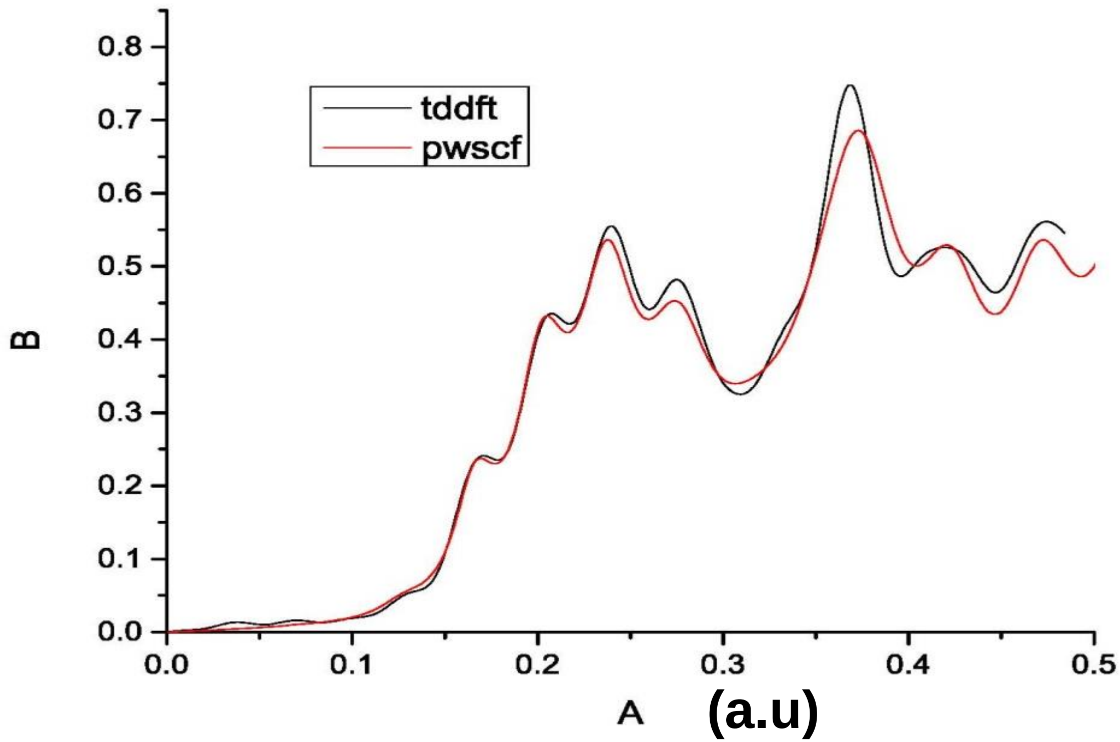
t_1 $t_2=t_1+1fs$

Excited state cooling in a 100 Al atom cluster



Total energy conservation

Optical absorption calculation



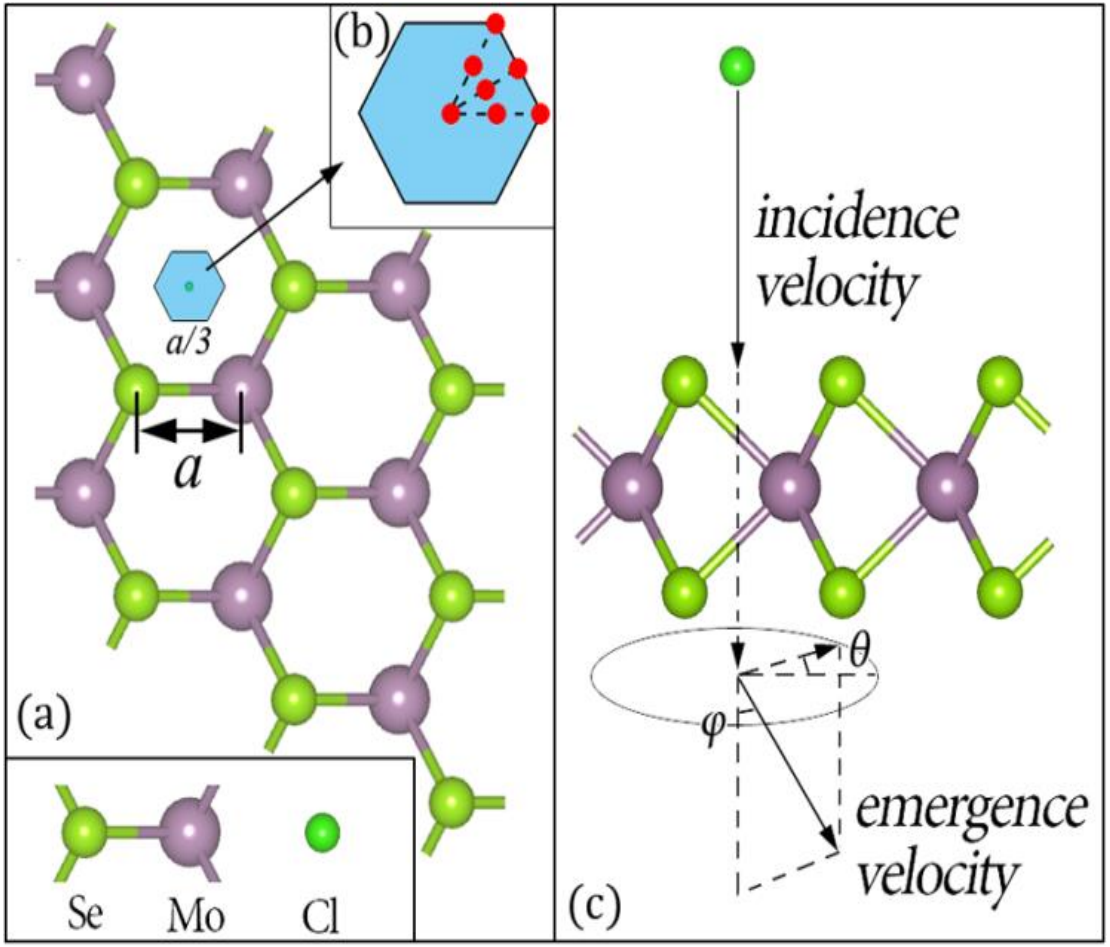
(a.u)

New method: rt-tddft

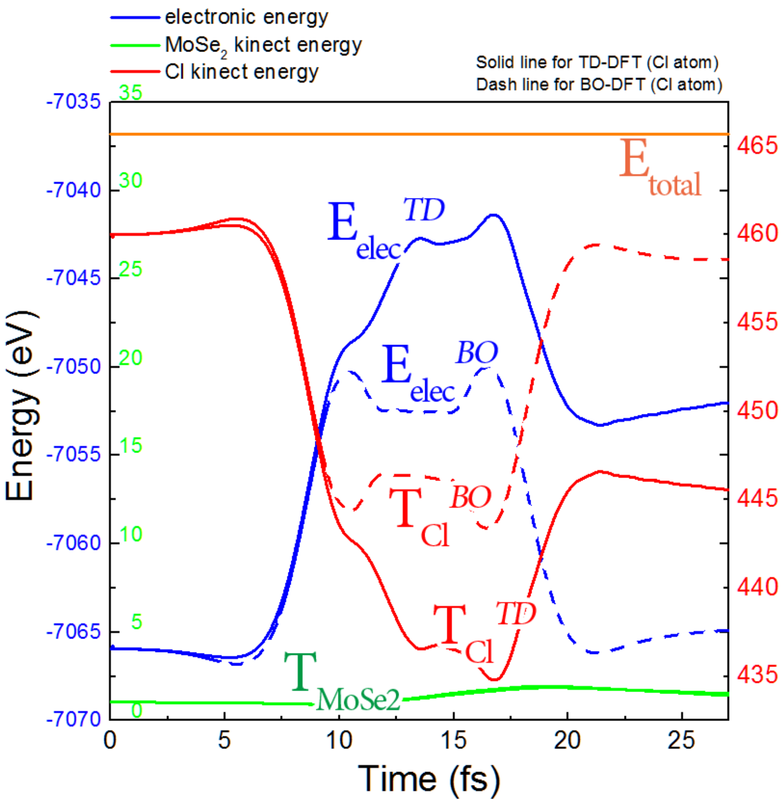
PWscf: perturbativ TDDFT

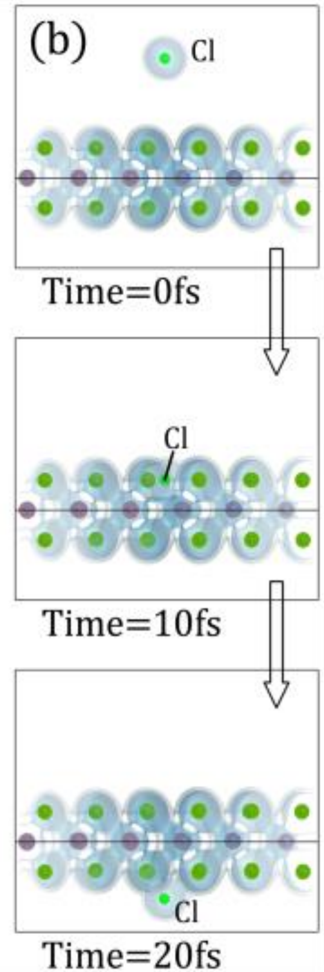
50 atom Au nanocluster

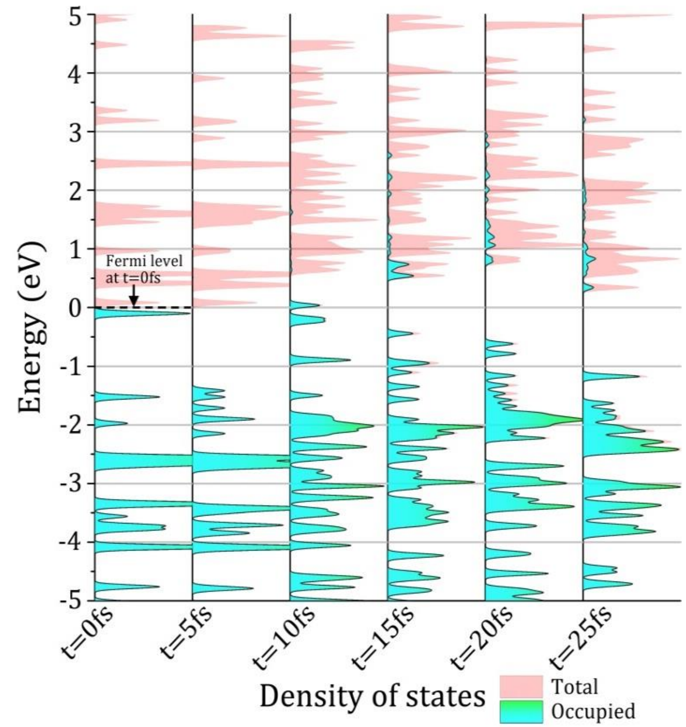
A Cl^- ion colliding on $MoSe_2$



Kinetic and potential energies





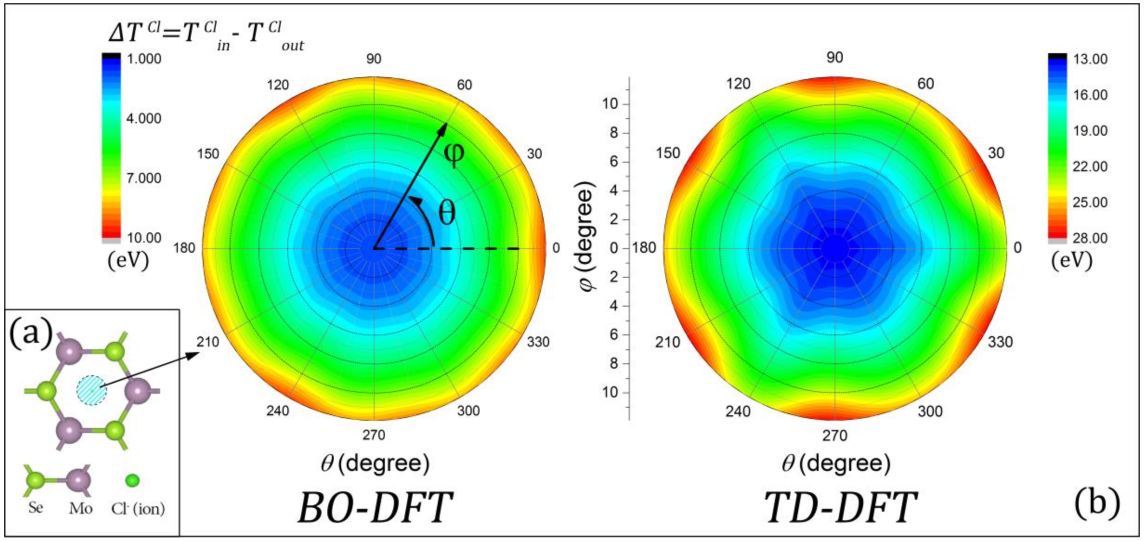


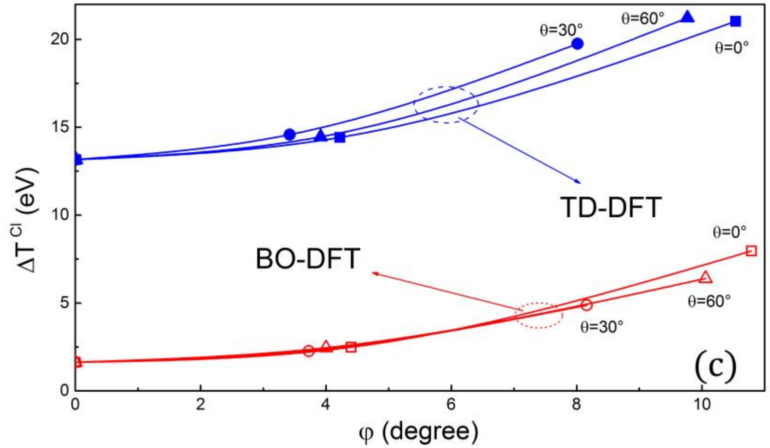
TD: rt-TDDFT:

BO: Born-Oppenheimer

(Wang, et.al, P.R.L, 114, 063004 (2015))

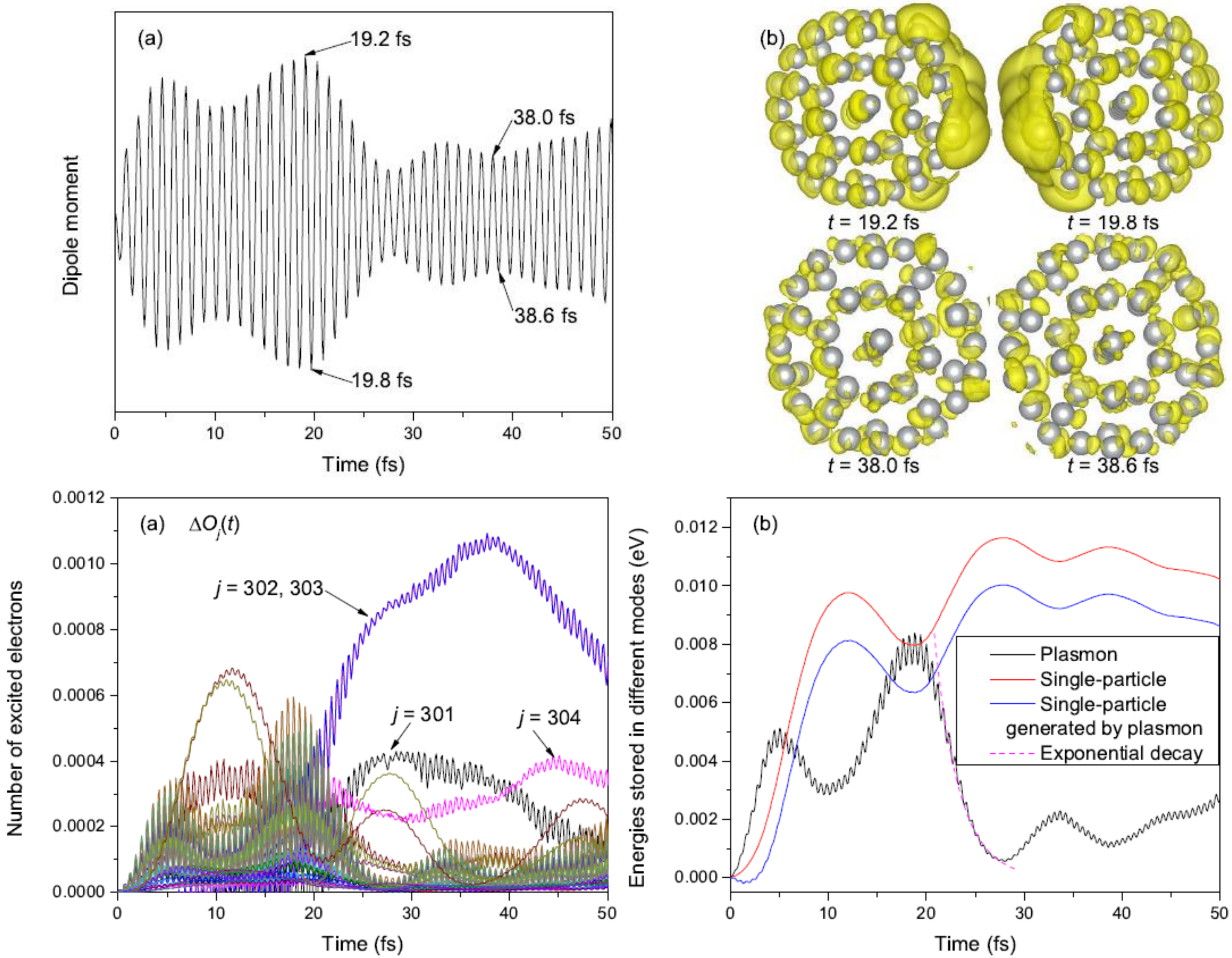
The energy lose of the Cl ion in different simulations





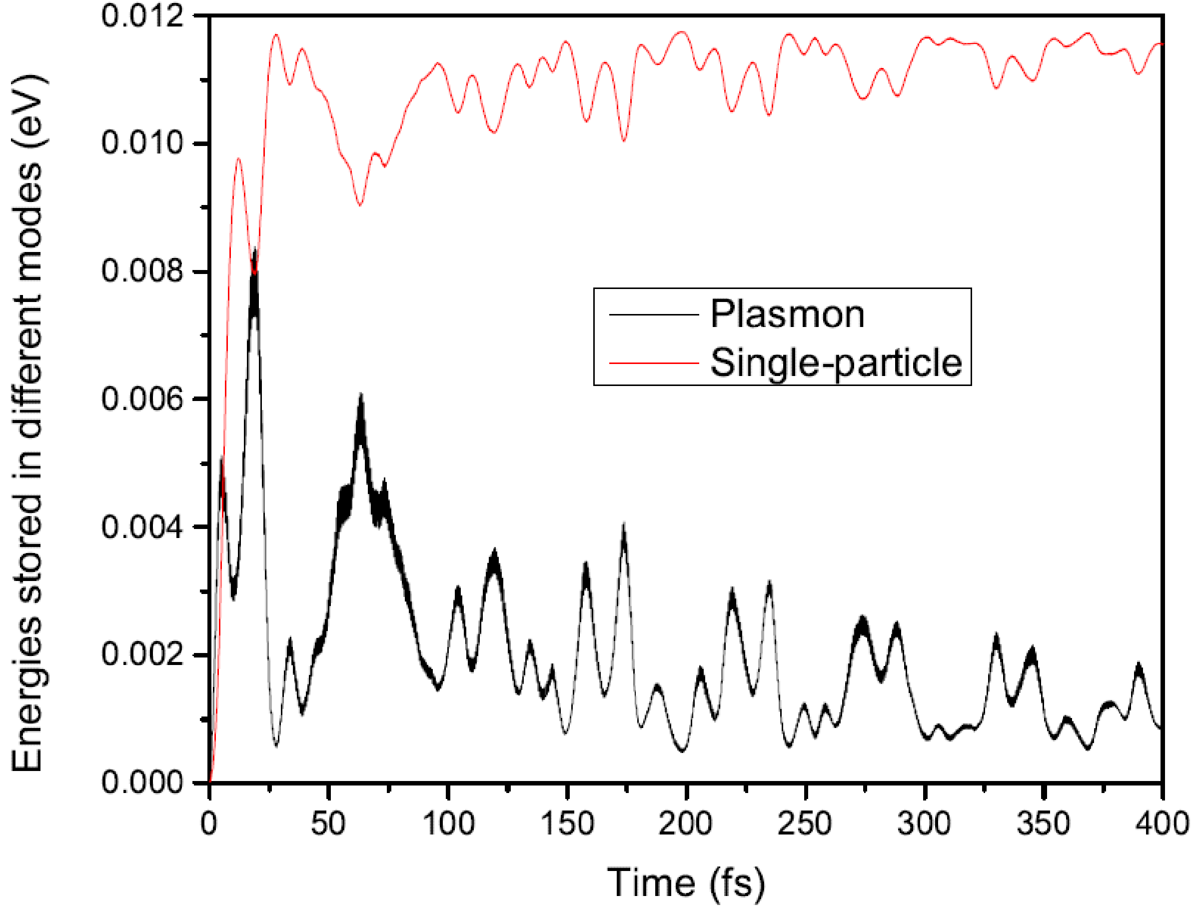
Cl- kinetic energy loss as a variable of scatter angle θ and φ, TD-DFT results compare with BO-DFT

Rt-TDDFT simulation of plasmon in Au55



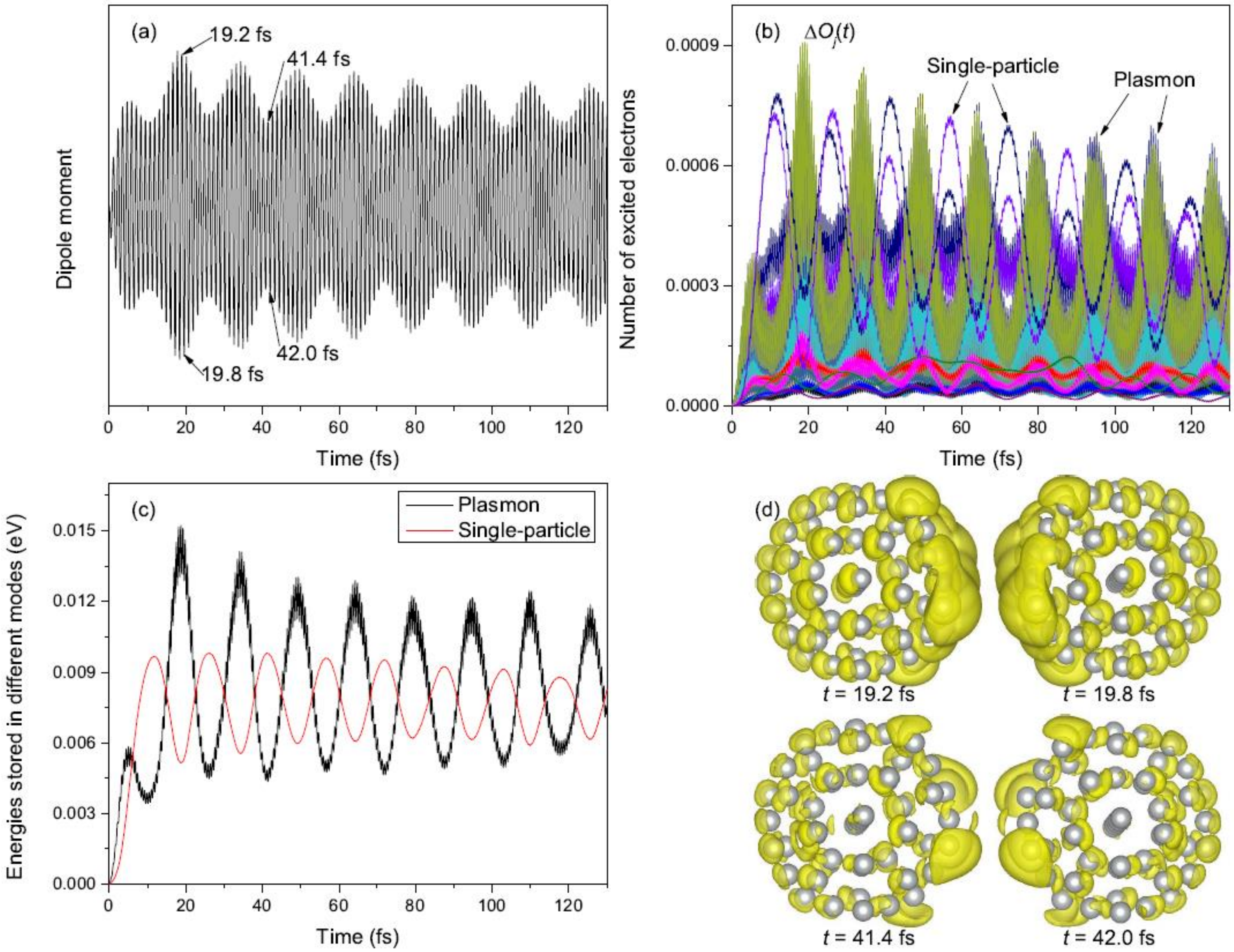
Energy flow from plasmon to single particle excitation

- 400 fs, no strong energy back-flow



(Ma, et.al, Nat. Comm. in press)

Rabi oscillation when there is no resonance between plasmon mode and single particle excitation energy



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GPU speed up for plane wave DFT calculations

- The rt-TDDFT is still very time consuming
- Typical dt~0.05 to 0.1 fs, each step ~4 leapfrog iterations
- For a ~100 atom system, it might take a few minutes with 200-400 CPUs

**GPU calculation can be very helpful:
reduce the time to 0.5min/step on a 4 GPU workstation
(takes 15 hours to finish a 100 fs run).**

Conclusion

- Charge patching method can be used to study single phonon assisted hopping transport in organic system (weak interation)

- Marcus theory can be used to calculate many charge transfer problems

- A variational method to calculate all the electron-phonon coupling constants, and to calculate the nonradiative recombination rate

- Nonadiabatic MD coupled with charge patching method can be used to study phonon-assisted electron transport problems for systems with thousands of atoms

- The new rt-TDDFT algorithm can be used to study problems with ~100 atoms for up to 1 ps.

- GPU can significantly speed up the plane wave DFT calculation (4 GPU Mstation can be a good solution for many groups).